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STUDIES OF π-BONDING BY X-RAY CRYSTAL STRUCTURE ANALYSIS

by

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Submitted to the University of Glasgow

for the degree of Doctor of Philosophy.

Chemistry Department

Faculty of Science

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PREFACE

The work described in this thesis was carried out under the supervision of Professor D.W.J. Cruickshank. I am grateful to him for his encouragement and many stimulating discussions during the course of the work. I should like to thank Professor J.M. Robertson for providing equipment for the experimental part of the work, and Professor J.S. Anderson, on whose good advice I took the decision to work at Glasgow.

Dr. M.R. Truter carried out some of the calculations at the University of Leeds, using Pegasus computer programmes, and I am grateful to her for this assistance. I should also like to thank Drs. J.S. Rollett, J.G. Sime, and W.E. Oberhansli, and Messrs. J.G.F. Smith, K.W. Muir, and D.R. McGregor for making available to me their computer programmes.

Financial support for the first two years of the work was provided by a grant from D.S.I.R.

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Summary.

STUDIES OF π-BONDING BY X-RAY CRYSTAL STRUCTURE ANALYSIS

by W.S. McDONALD

X-ray crystal structure analyses and refinements are described of six compounds having structures in which a second-row element (aluminium, silicon, phosphorus, or sulphur) is bonded to four atoms of a first-row element (nitrogen or oxygen). The dimensions of molecules and ions of this type provide information leading to an improved understanding of the π-bonding in compounds of the second-row elements. Least-squares refinement was used in each case to obtain atomic co-ordinates and molecular dimensions, together with the estimated standard deviations of these quantities.

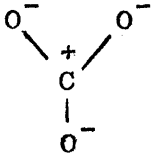
The crystal structure of a new type of aluminium-nitrogen compound was determined, and the molecular structure elucidated. The results of this analysis confirm the absence of p-p π-bonding in this compound. The crystal structures of two silicates, sodium metasilicate and the zinc mineral hemimorphite, were refined with some accuracy, providing detailed dimensions of the silicon-oxygen structures of these compounds. The structure of sodium pyrophosphate decahydrate has been refined to provide accurate dimensions of the pyrophosphate ion, permitting a comparison with other iso-electronic ions and molecules. The The crystal structure of dipotassium ethyl phosphate tetrahydrate was determined, but a high degree of pseudo-symmetry prevented the analysis from yielding accurate dimensions for the ethyl

phosphate anion. Published data on the trimeric modification of sulphur trioxide were subjected to further refinement. Certain anomalous features of the original structure dissappeared on refinement, and a comparison with iso-electronic phosphorus and silicon structures was made. The work concludes with a general discussion of the results, taken together with other recently published work which is relevant to the theory of π-bonding.

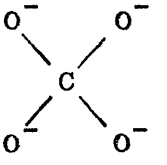
Chapter 1

INTRODUCTION

The occurrence of π-bonding in compounds of the first row elements is very common. The oxy-anions BO_3^{3-}, CO_3^{2-}, and NO_3^- are known to have trigonal planar structures with short X-O bonds due to p-p π-bonding. The ortho-anions, CO_4^{4-} and NO_4^{3-}, where π-bonding cannot occur because of lack of available orbitals, are not known. The fluoro-complexes, BeF_4^{2-}, BF_4^-, and CF_4 are known, however. The effect of π-bonding in the carbonate ion, for instance, would be to redistribute the formal charges of the σ-bonded structure, I, to produce a more uniform distribution of charge. For the ortho-carbonate ion, II, however the absence of π-bonding would prevent such



I



II

a redistribution of charge. It is perhaps this lack of π-bonding potentiality which accounts for the non-existence of ortho-carbonate and ortho-nitrate ions.

Turning to the oxy-anions of the second row elements we find that SiO_4^{4-}, PO_4^{3-}, SO_4^{2-}, and ClO_4^- are stable species, although in going from chlorine to silicon there is an increasing tendency to form

poly-anions, with a consequent lowering of the negative charge on each tetrahedral unit of the structure.

In the compounds of the first row elements, the orbitals of suitable energy for bonding are the 2s and 2p orbitals, and any π-bonds formed must make use of the p-orbitals. For the second row elements we have to consider the use of 3d orbitals for bonding in addition to the 3s and 3p orbitals. We would expect that in tetrahedral species the 3s and 3p orbitals would be used for σ-bonding and any π-bonding would therefore have to utilise the 3d orbitals. In structures where the second row element forms less than four σ-bonds, the use of both 3p and 3d orbitals for π-bonding is possible. Many thio-analogues of π-bonded oxygen compounds are known, in which p-p π-bonding could occur in the same way as it does in the oxygen compounds. The use of 3d orbitals in addition cannot be ruled out, however. In a molecule such as SO_3, with a trigonal planar structure, both 3p and 3d orbitals probably participate in the π-bonding. For phosphorus there is little evidence of p-p π-bonding. The best characterised example is the molecule HCP, with a short P-C bond. For silicon there is no known example of p-p π-bonded compound. All attempts to prepare aluminium compounds

analogous to the π-bonded boron compounds, such as the borazoles, have given instead polymeric structures with 4 co-ordinate aluminium. There is clearly a much lower tendency for second row elements to form p-p π-bonds. The simplest explanation of this is that the increase in covalent radii prevents sufficient p-p π-overlap for effective bonding to take place. The increasing covalent radius in going from sulphur to silicon would therefore explain the absence of p-p π-bonding in silicon compounds. In the HCP molecule, the additional bond-shortening produced by a second p-p π-bond system probably allows sufficient overlap for a stable multiple bond to exist.

The shapes and sizes of d-orbitals, however, would seem to permit satisfactory π-overlap to occur when p-p π-overlap is poor. It was shown by Cruickshank (1961) that the bond lengths and bond length variations in tetrahedral molecules of second row elements can be explained by considering d-p π-bonding. He showed that in a tetrahedral anion such as SO_4^{2-}, the symmetry of the d-orbitals is such as to permit the formation of two strongly π-bonding molecular orbitals by overlap with the lone pair p-orbitals on the oxygen atoms. Attachment of another group to one or more of the oxygen

atoms then reduces the availability of p-orbitals on those oxygens, and this leads to a change in the π-bond orders for the tetrahedral X-O bonds. The observed bond lengths in a wide range of tetrahedral compounds of second row elements were rationalised on this basis.

Accurate dimensions were not available, however, for certain key compounds which would provide a test of the adequacy of this theory, and which might indicate ways in which the simple theory could be improved. The structural studies described in the following chapters were undertaken in order to provide some of this information.

Reference

CRUICKSHANK, D.W.J. (1961), J. Chem. Soc., 5486.

Chapter 2

THE CRYSTAL STRUCTURE OF $Al_4N_4(C_6H_5)_8$

There have been several attempts to prepare aluminium analogues of the borazenes, $R_2B = NR_2$, and of the borazoles $(R\text{-}B\text{-}N\text{-}R)_3$. The monomeric borazenes are iso-electronic with ethylenes, and are believed to be π-bonded in the same way. A monomeric borazyne, R-B = N-R, is known, which probably has a structure similar to the corresponding acetylene, whilst the stable trimeric borazoles exhibit aromatic properties and resemble the corresponding benzene derivatives.

All earlier attempts to obtain the corresponding aluminium compounds yielded instead high molecular weight materials in which it was assumed that the aluminium was 4 co-ordinate. However, Jones and McDonald (1962), by working in dilute solution, were able to obtain soluble compounds having the stoichiometry expected for borazole analogues. Their compounds were of general formula (ArN.AlPh)n, where n would be 3 if the compounds were of the borazole type. Their molecular weight measurements showed, however, that the compounds were tetrameric. This did not rule out the possibility of a π-bonded structure, though, since

tetrameric borazynes, iso-electronic with cyclo-octatetraene derivatives, have been synthesised (Turner and Warne, 1962).

In order to establish the molecular structure of these compounds, a crystal structure analysis of the octaphenyl compound, $Al_4N_4(C_6H_5)_8$, was carried out.

Crystal Data

$Al_4N_4C_{48}H_{40}$, M = 780·8. Tetragonal, a = 19·93 Å, c = 10·82 Å, U = 4298 Å^3, D_m = 1·20, D_c = 1·206 for Z = 4. Space group $I4_1/a$ (No. 88). Molecular symmetry $\bar{4}$. Absorption coefficient for x-rays of wavelength λ = 1·542 Å, μ = 12·9 cm.$^{-1}$

Data Collection

Well formed single crystals were obtained by slow cooling of a saturated solution in benzene. The crystals were colourless tetragonal bipyramids. Because of their extreme sensitivity to oxygen and moisture they were transferred under nitrogen and sealed in Lindemann glass tubes. Cell dimensions and space group were determined from equi-inclination Weissenberg photographs.

3-dimensional data were obtained by visual estimation of equi-inclination Weissenberg photographs of the reciprocal lattice layers Okl to 13kl, taken with Cu Kα radiation. Data from different layers were correlated by means of the common reflections, to give 733

independent intensities on a single scale. These were corrected for Lorentz and polarisation factors; absorption was neglected.

Structure Determination

The space group requires that the molecules have $\bar{4}$ symmetry, and the asymetric unit is one quarter of a molecule, so that aluminium, nitrogen, and twelve carbon atoms have to be located. Two possible structures were considered more likely; either an eight-membered ring of alternating aluminium and nitrogen atoms, or a cube with aluminium and nitrogen at alternate corners. The 3-dimensional Patterson function was computed, and from this the cube shape of the molecule was at once evident. Most prominent were the fourfold Al-N peaks of the cube edge, and the Al-Al and N-N face diagonal peaks of double weight were also prominent. The single weight Al-N body diagonal vector was not resolved. From these peaks the co-ordinates of the Al and N positions were obtained, although it was not clear which atom was in which site.

Trial co-ordinates of the four carbon atoms C(1), C(4), C(7) and C(10) were obtained by assuming that the Al-C and N-C bonds were collinear with the cube diagonals and were equal in length to their expected mean. A structure factor calculation using these

co-ordinates gave a residual ($R = \sum|K F_o - |F_c|| / \sum K F_o$) of 0·492 for one arrangement of the aluminium and nitrogen atoms, and R = 0·502 with Al and N interchanged. The small difference between the two sets was rather surprising, but the reason became apparent during the refinement when partial disorder of the Al and N atoms was found.

A 3-dimensional Fourier synthesis was then computed using the phases given by the set of calculated structure factors having R = 0·492. The remaining 8 carbon atoms were located from the electron density map, and a structure factor calculation using these co-ordinates gave R = 0·287. A further Fourier and structure factor calculation reduced the residual to 0·245.

Least Squares Refinement

The atomic co-ordinates and anisotropic temperature factors were refined using the structure-factor and least-squares programme written by J.S. Rollett for the Deuce computer. The weighting scheme used was $\sqrt{w} = 1$ for $K F_o \leq 80$, $\sqrt{w} = 80/K F_o$ for $K F_o > 80$. $\sum w(K F_o - |F_c|)^2$ was minimised. Unobserved reflections were not included, and the 420 reflection which seemed to be affected by extinction was omitted. Twelve cycles produced convergence and reduced the residual to

0120. This refinement produced temperature factors for the nitrogen atom much lower than those of the other atoms. The U_{ij} of nitrogen were equivalent to an isotropic value of B = 1·99, and those of aluminium to B = 4·34. Since these atoms are bonded together and are equidistant from the molecular centre, we should expect them to have very nearly equal temperature factors. The large difference obtained suggests that there is some disorder, with Al and N atoms interchanged between their respective sites, together with a positional disorder of the carbon atoms caused by the 0·4 Å difference between the Al-C and N-C bond lengths. Low temperature factors for N and high ones for Al would then be produced in the refinement to compensate for the inappropriate scattering curves used. There would also be high temperature factors for the carbon atoms because of their positional disorder.

The fact that the temperature factors for Al and N should be approximately equal was made the basis for the estimation of the amount of disorder. For an initial calculation 10% interchange was assumed. The scattering curves for Al and N were replaced by those of 0·9 Al + 0·1 N and 0·9 N + 0·1 Al, and isotropic temperature factors of B = 3·64 were substituted for both atoms. Two cycles of least-squares refinement were carried out,

with the parameters of Al and N as the only variables. These produced shifts of the temperature factors towards their previous values, indicating that the degree of interchange was greater than 10%. By estimating the values to which the temperature factors were converging 15% interchange was judged more appropriate. Two further cycles of least-squares were carried out using 0·85 + 0·15 scattering curves and with all parameters as variables. As starting parameters for these cycles the Al and N temperature factors were allowed to retain their anisotropy, but with their mean isotropic values made equal. This produced only very small shifts of the temperature factors in the opposite directions to those in the previous two cycles, and reduced the residual to 0·111. It was concluded that the value of 15% for the interchange was close to the true value. The final co-ordinates and their estimated standard deviations (calculated from the diagonal elements of the least-squares matrix) are given in Table 1. The temperature factors and their standard deviations are given in Table 2, and the observed and calculated structure factors are listed in Table 3.

TABLE 1

FINAL FRACTIONAL CO-ORDINATES
(E.S.D.s IN BRACKETS ARE IN UNITS IN THE 4th PLACE)

ATOM	x	y	z
.85 Al + .15 N	0.0342(2)	0.1917(2)	0.0363(4)
.85 N + .15 Al	0.0341(4)	0.1917(4)	0.2148(8)
C(1)	0.0713(7)	0.1289(7)	-0.0708(13)
C(2)	0.0675(9)	0.1447(9)	-0.1965(15)
C(3)	0.0899(11)	0.0990(10)	-0.2876(18)
C(4)	0.1177(9)	0.0396(9)	-0.2515(16)
C(5)	0.1243(10)	0.0204(9)	-0.1294(18)
C(6)	0.0995(9)	0.0678(8)	-0.0373(16)
C(7)	0.0648(6)	0.1362(6)	0.2841(12)
C(8)	0.0297(8)	0.0752(7)	0.2949(15)
C(9)	0.0574(9)	0.0199(9)	0.3543(16)
C(10)	0.1238(9)	0.0262(8)	0.4062(13)
C(11)	0.1591(9)	0.0873(8)	0.3932(15)
C(12)	0.1287(7)	0.1421(8)	0.3318(12)

TABLE 2

TEMPERATURE FACTORS
(E.S.D.s GIVEN IN BRACKETS ARE UNITS IN THE 3rd PLACE)

ATOM	U11	U22	U33	2U23	2U31	2U12
.85 Al + .15 N	0.050(2)	0.045(2)	0.045(2)	-0.008(3)	0.002(3)	0.002(3)
.85 N + .15 Al	0.048(3)	0.049(3)	0.045(3)	-0.002(6)	-0.009(6)	0.017(6)
C(1)	0.065(6)	0.074(6)	0.068(6)	-0.019(11)	0.008(11)	-0.019(11)
C(2)	0.099(8)	0.110(8)	0.086(8)	0.002(15)	0.033(14)	-0.023(14)
C(3)	0.150(11)	0.134(11)	0.108(9)	0.049(18)	0.069(18)	0.028(18)
C(4)	0.108(8)	0.141(9)	0.081(8)	-0.030(15)	0.066(14)	-0.088(15)
C(5)	0.137(10)	0.091(8)	0.126(10)	-0.012(17)	0.075(19)	-0.012(16)
C(6)	0.119(9)	0.062(7)	0.102(8)	-0.017(14)	0.013(16)	0.019(13)
C(7)	0.058(5)	0.062(6)	0.053(5)	-0.060(9)	0.017(10)	0.019(9)
C(8)	0.103(8)	0.042(6)	0.107(8)	-0.010(12)	0.009(15)	0.016(11)
C(9)	0.110(9)	0.097(8)	0.105(9)	0.008(16)	0.052(15)	0.023(14)
C(10)	0.153(10)	0.085(7)	0.057(7)	-0.034(12)	0.019(14)	0.050(14)
C(11)	0.124(9)	0.081(7)	0.088(8)	-0.059(13)	-0.014(15)	0.050(13)
C(12)	0.067(6)	0.097(7)	0.057(6)	-0.018(11)	0.005(10)	0.064(11)

TABLE 3

OBSERVED AND CALCULATED STRUCTURE FACTORS

H	K	L	Fo	Fc	H	K	L	Fo	Fc	H	K	L	Fo	Fc	H	K	L	Fo	Fc
0	0	4	94.6	95.5	1	8	3	23.7	-26.5	3	3	4	70.9	70.9	4	13	7	26.4	19.5
0	0	8	40.9	-39.1	1	8	5	80.2	-83.3	3	3	6	86.1	94.6	4	14	0	55.4	55.8
0	0	12	29.0	-31.8	1	8	7	16.6	16.0	3	3	8	31.2	28.8	4	14	4	11.8	19.8
0	1	1	163.4	-178.6	1	8	11	26.4	27.4	3	4	3	61.4	-58.3	4	15	3	20.4	21.5
0	1	3	135.4	131.1	1	9	2	76.6	75.5	3	4	5	23.7	-28.5	4	17	5	20.5	-16.0
0	1	5	60.3	-53.7	1	9	4	42.6	-35.3	3	4	7	11.8	-20.4	4	17	7	33.5	-14.3
0	1	7	50.2	-45.4	1	9	6	71.9	71.1	3	5	2	20.4	14.9	4	18	0	47.3	-44.0
0	1	11	26.4	-34.5	1	9	8	20.5	-19.8	3	5	4	62.6	-71.7	4	18	4	26.4	-21.1
0	2	0	175.4	-202.4	1	9	10	16.6	23.1	3	5	6	29.0	-22.0	4	19	1	31.2	24.7
0	2	2	87.6	-87.7	1	10	1	93.0	95.7	3	5	8	33.5	-33.0	4	19	5	16.6	20.9
0	2	4	158.7	-155.0	1	10	5	75.6	70.8	3	6	1	44.2	43.4	4	19	7	23.6	17.5
0	2	6	23.7	-17.5	1	10	7	37.5	-42.5	3	6	3	20.5	-21.6	4	20	0	50.1	50.6
0	2	8	47.3	42.4	1	11	2	40.9	-40.7	3	6	5	70.9	73.3	4	20	2	37.4	5.0
0	2	12	26.4	31.9	1	11	4	44.2	39.3	3	6	7	20.5	-26.8	4	20	4	23.6	18.0
0	3	1	129.0	120.2	1	11	6	90.0	-99.6	3	7	2	20.4	17.8	4	21	1	11.8	-17.5
0	3	3	26.4	-30.2	1	11	10	20.5	-29.1	3	7	4	26.4	-35.2	4	21	5	16.7	-18.5
0	3	5	81.9	77.9	1	12	1	50.2	-51.7	3	7	6	75.7	-76.4	4	22	0	29.0	-29.3
0	3	7	47.3	44.3	1	12	3	16.6	11.9	3	8	1	67.0	-65.0	4	23	1	20.4	17.7
0	4	0	207.5	-203.2	1	12	5	47.3	-46.0	3	8	3	26.4	25.7	5	1	2	56.6	-46.7
0	4	2	50.1	36.4	1	12	7	35.4	37.6	3	8	5	63.6	-60.6	5	1	4	99.0	-95.3
0	4	4	35.4	28.8	1	13	2	50.1	55.8	3	8	7	48.7	44.8	5	1	6	11.8	-15.6
0	4	6	23.7	-24.2	1	13	6	29.0	26.6	3	8	11	20.4	19.0	5	1	8	31.4	-27.7
0	4	8	16.6	12.1	1	14	1	29.0	28.8	3	9	2	93.0	92.2	5	2	1	126.3	-128.4
0	5	1	33.3	23.5	1	16	1	23.6	25.3	3	9	4	23.6	18.7	5	2	3	40.9	-35.8
0	5	3	74.8	-63.4	2	1	1	153.7	-149.2	3	9	6	81.0	87.7	5	2	5	45.7	42.9
0	6	0	156.9	148.2	2	1	3	132.2	-129.5	3	9	8	16.6	19.5	5	2	7	11.8	-14.9
0	6	2	23.6	25.8	2	1	5	48.7	-44.4	3	9	10	35.4	36.0	5	2	9	23.6	23.9
0	6	4	16.6	16.4	2	1	7	52.9	-48.9	3	10	1	98.2	92.1	5	3	4	39.3	-32.7
0	6	6	16.6	10.3	2	1	9	23.7	-20.2	3	10	5	60.3	51.7	5	3	6	29.0	-26.9
0	6	8	16.7	-15.0	2	2	0	82.0	-88.3	3	10	7	45.8	-42.5	5	3	8	48.7	51.5
0	7	1	75.7	-75.6	2	2	2	122.2	118.4	3	11	2	115.3	-112.6	5	4	1	60.3	64.0
0	7	3	31.2	-24.6	2	2	4	95.3	-86.4	3	11	6	86.9	-104.1	5	4	3	91.5	90.1
0	7	5	29.0	-25.2	2	2	6	16.6	15.7	3	11	10	29.0	-33.1	5	5	2	29.0	29.6
0	7	7	37.4	-35.5	2	3	1	72.8	72.9	3	12	1	40.9	-39.0	5	5	4	37.4	-34.6
0	8	0	74.8	-70.1	2	3	3	90.8	83.5	3	12	3	11.8	11.0	5	5	6	48.7	45.8
0	8	2	44.2	-45.3	2	3	5	97.4	108.2	3	12	5	56.6	-56.8	5	6	1	77.6	75.8
0	8	4	89.3	-81.9	2	3	7	35.4	27.4	3	12	7	31.2	18.8	5	6	3	55.5	-59.6
0	8	8	20.4	14.8	2	3	9	35.4	34.7	3	13	2	23.6	22.7	5	6	7	20.5	-19.2
0	8	12	16.6	23.4	2	4	0	153.3	-178.5	3	13	6	62.5	66.9	5	7	2	82.0	-89.5
0	9	1	59.1	54.4	2	4	2	55.5	-40.6	4	1	3	35.4	30.0	5	7	4	16.6	19.5
0	9	3	20.5	-3.7	2	4	4	61.4	-51.5	4	1	5	87.6	-92.0	5	7	6	51.6	-48.8
0	9	5	60.3	62.9	2	4	6	61.4	59.5	4	1	7	23.7	-14.8	5	7	8	31.2	-29.6
0	9	7	31.2	33.6	2	4	8	26.4	26.8	4	1	9	26.4	-23.3	5	7	10	23.7	-22.0
0	10	0	107.0	105.3	2	5	1	16.6	14.3	4	2	0	233.7	-424.2	5	8	1	45.8	-40.1
0	10	2	35.4	36.2	2	5	3	20.5	-16.1	4	2	2	63.6	59.9	5	8	5	35.5	-28.5
0	10	4	20.4	15.8	2	5	5	48.7	-48.4	4	2	4	39.3	-34.7	5	8	7	51.5	50.0
0	11	1	16.7	-19.3	2	5	7	11.8	-12.2	4	2	6	11.8	19.9	5	9	2	11.8	7.5
0	11	5	37.4	-37.3	2	6	0	57.9	46.5	4	2	8	20.5	-10.9	5	9	4	37.4	33.3
0	11	7	31.2	-32.3	2	6	2	11.8	-0.9	4	3	1	103.1	-134.2	5	9	6	76.6	75.2
0	12	0	97.4	-89.4	2	6	4	37.4	32.5	4	3	3	52.9	-47.5	5	9	8	20.4	18.8
0	12	2	11.8	-6.2	2	6	6	11.8	20.8	4	3	5	20.4	20.5	5	9	10	23.6	28.2
0	12	4	33.5	-36.0	2	6	8	31.2	-30.0	4	4	2	45.7	48.2	5	10	1	56.6	56.2
0	13	1	35.4	32.9	2	7	1	82.0	-79.3	4	4	4	11.8	12.3	5	10	5	57.9	54.7
0	13	3	45.8	-46.3	2	7	3	33.5	-26.7	4	4	6	11.8	-16.8	5	10	7	31.2	-20.8
0	13	5	16.6	11.9	2	7	5	65.9	-61.3	4	4	8	16.7	-21.5	5	11	2	52.9	-49.4
0	13	7	33.4	42.9	2	7	7	23.7	-26.9	4	5	1	82.8	-78.2	5	11	4	20.5	-24.1
0	14	2	26.4	-27.2	2	8	0	181.6	-209.2	4	5	3	35.4	27.4	5	11	6	60.3	-60.9
0	14	4	37.4	31.1	2	8	2	11.8	10.1	4	5	5	60.3	59.9	5	11	8	16.6	22.9
0	15	1	33.5	-31.8	2	8	4	56.6	-52.9	4	5	7	20.5	-20.6	5	11	10	20.5	-22.3
0	15	3	20.4	14.7	2	8	6	16.7	-19.7	4	5	9	23.7	-24.8	5	12	1	33.5	-28.7
0	16	0	16.6	17.9	2	8	12	16.6	14.5	4	6	0	74.7	78.3	5	12	3	20.5	-21.0
0	16	2	37.4	39.9	2	9	1	89.2	79.3	4	6	2	45.8	-46.5	5	12	5	42.6	-43.4
0	18	0	37.4	-36.8	2	9	3	11.8	-8.4	4	6	4	47.3	43.2	5	13	2	23.6	20.7
0	20	0	23.7	-21.1	2	9	5	73.8	77.8	4	7	1	80.2	-77.6	5	13	6	31.2	31.4
1	1	2	91.5	82.2	2	9	7	33.4	31.9	4	7	3	44.2	37.4	5	14	1	20.4	14.0
1	1	4	45.7	27.9	2	9	11	23.6	25.6	4	7	5	64.8	-59.8	5	14	3	23.6	24.7
1	1	6	81.0	-83.2	2	10	0	64.8	73.3	4	7	7	11.8	-16.7	5	15	6	23.6	25.1
1	1	10	40.9	-47.3	2	10	2	35.4	31.7	4	7	9	26.4	-25.7	5	16	3	16.7	-20.6
1	2	1	132.2	-156.9	2	10	4	96.7	96.6	4	8	0	118.3	-123.2	5	16	5	23.6	17.3
1	2	3	107.0	-96.2	2	11	1	83.6	-76.3	4	8	2	59.1	58.6	5	17	2	23.7	-21.4
1	2	5	120.6	-119.9	2	11	5	58.0	-59.0	4	8	4	44.2	-36.5	5	17	6	31.2	-33.4
1	2	7	57.9	55.8	2	11	7	20.5	-24.6	4	8	6	23.6	30.0	5	18	1	23.7	-24.5
1	3	2	305.6	348.0	2	12	0	60.3	-63.6	4	8	8	11.8	8.2	5	18	7	20.4	17.7
1	3	4	29.0	19.0	2	12	2	16.6	8.4	4	8	12	11.8	15.5	5	19	6	20.4	21.7
1	3	6	61.4	61.4	2	12	4	40.9	-36.5	4	9	1	85.2	87.9	5	20	1	31.2	36.8
1	3	8	29.0	-11.8	2	12	6	16.6	19.0	4	9	3	39.3	-37.2	5	20	5	20.4	16.0
1	4	1	50.1	46.3	2	13	1	42.6	34.1	4	9	5	62.5	62.2	5	21	6	16.7	-19.8
1	4	3	65.9	-60.8	2	13	3	20.5	-12.0	4	9	7	54.1	52.6	6	1	1	87.6	-80.8
1	4	5	96.7	98.6	2	13	5	37.4	35.5	4	9	11	11.8	21.0	6	1	3	57.9	49.8
1	4	7	16.7	-22.8	2	13	7	33.6	19.5	4	10	0	76.6	78.7	6	1	5	11.8	12.4
1	4	9	20.4	20.1	2	14	0	29.0	29.9	4	10	2	20.5	-24.2	6	2	2	54.2	-51.8
1	5	2	16.7	-19.8	2	14	2	33.5	-33.8	4	10	4	74.7	69.2	6	2	4	55.5	-44.6
1	5	6	69.0	-65.0	2	14	4	31.2	37.9	4	10	6	11.8	-3.0	6	2	6	11.8	11.1
1	6	1	42.6	45.6	3	1	2	39.3	-41.3	4	11	1	55.5	-59.0	6	2	8	23.6	27.1
1	6	3	56.6	50.7	3	1	4	50.2	-40.0	4	11	5	59.2	-57.5	6	3	1	110.9	-111.9
1	6	5	11.8	15.7	3	1	6	89.3	-89.6	4	11	7	47.3	-38.9	6	3	3	16.6	11.3
1	6	7	11.8	-22.6	3	1	10	20.5	-23.1	4	12	0	60.3	-61.7	6	3	5	47.3	-40.8
1	6	9	20.4	25.3	3	2	1	90.8	-93.9	4	12	2	16.7	-13.5	6	4	0	125.1	136.1
1	7	2	20.4	13.6	3	2	3	29.0	20.1	4	12	6	11.8	-18.9	6	4	2	70.9	75.8
1	7	4	11.8	-15.9	3	2	5	65.9	-61.1	4	13	1	29.0	28.4	6	4	4	39.2	37.2
1	7	6	33.5	-34.5	3	2	9	31.2	28.3	4	13	3	29.0	27.0	6	4	6	23.7	-15.1
1	8	1	141.9	-132.5	3	3	2	31.2	-29.2	4	13	5	47.3	38.8	6	4	8	20.5	-21.9

TABLE 3

(CONTINUED)

H	K	L	Fo	Fc	H	K	L	Fo	Fc	H	K	L	Fo	Fc	H	K	L	Fo	Fc
6	5	3	55.5	-59.4	8	2	6	35.5	-30.8	10	4	4	26.4	19.0	12	11	3	16.6	16.7
6	6	0	16.7	-15.2	8	3	3	11.8	24.3	10	5	1	11.8	7.2	12	11	5	20.4	21.3
6	6	2	29.0	-30.0	8	3	5	37.4	30.0	10	5	5	26.4	-23.1	12	12	0	29.0	23.2
6	6	4	57.9	50.0	8	4	0	81.9	83.8	10	6	0	118.3	-141.7	12	14	0	23.6	19.3
6	6	6	59.2	-55.9	8	4	2	11.8	16.2	10	6	2	11.8	-8.9	12	16	0	33.5	-29.3
6	7	1	11.8	6.4	8	4	4	37.4	33.5	10	6	4	45.8	-47.4	12	16	2	20.2	-16.9
6	7	3	48.7	46.2	8	5	1	52.8	55.5	10	6	6	20.4	13.6	12	18	0	29.0	27.6
6	7	5	11.8	13.8	8	5	3	16.7	-14.9	10	7	1	20.4	18.8	13	1	4	20.4	18.1
6	7	9	16.7	-16.3	8	5	5	47.3	-44.8	10	7	3	23.7	-22.3	13	2	1	11.8	14.7
6	8	0	80.2	-79.5	8	5	7	26.4	-23.2	10	7	5	37.4	33.0	13	2	3	35.4	33.3
6	8	2	16.6	19.0	8	6	0	29.0	18.6	10	7	7	23.6	19.2	13	3	2	29.0	34.8
6	8	4	23.7	-18.2	8	6	2	29.0	17.3	10	7	9	16.6	20.4	13	3	6	39.2	36.8
6	9	1	55.4	52.3	8	6	4	42.6	-37.3	10	8	0	68.9	63.6	13	4	1	23.6	19.8
6	9	5	47.3	45.0	8	7	1	60.3	59.2	10	8	2	11.8	11.0	13	4	5	23.6	18.6
6	10	0	118.2	131.0	8	7	3	20.4	16.5	10	8	4	29.0	29.7	13	4	7	26.4	-28.9
6	10	2	11.8	-3.9	8	7	5	26.4	27.9	10	9	1	33.5	-26.8	13	5	2	42.6	-43.1
6	10	4	26.4	31.1	8	7	7	20.4	16.4	10	9	3	11.8	15.7	13	5	6	50.2	-41.9
6	10	6	16.6	12.7	8	7	9	16.6	24.1	10	9	5	40.9	-38.1	13	6	1	48.7	-53.0
6	11	1	42.6	-40.9	8	8	0	40.9	-37.9	10	9	7	16.7	-17.2	13	6	3	23.7	-26.7
6	11	3	29.0	-22.0	8	8	4	23.7	-14.7	10	10	0	40.9	-44.0	13	6	5	35.5	-31.3
6	11	5	33.5	-25.1	8	9	1	23.6	19.5	10	10	4	23.7	-19.0	13	6	7	23.6	21.6
6	11	7	11.8	-16.2	8	9	3	26.4	-23.3	10	11	1	45.7	43.7	13	7	6	45.7	41.7
6	12	0	23.7	-20.7	8	10	0	23.6	19.6	10	12	0	23.6	25.3	13	8	1	40.9	38.2
6	12	2	37.4	-38.8	8	10	4	23.6	20.2	10	12	2	16.7	-18.1	13	8	3	31.2	30.1
6	12	4	51.6	-45.1	8	12	0	23.7	-25.6	10	12	4	16.6	17.1	13	8	5	44.2	45.5
6	12	6	26.4	-24.8	8	12	2	37.4	-34.3	10	13	1	31.2	-24.9	13	8	7	20.5	-19.5
6	13	1	33.4	22.3	8	13	1	16.7	-23.2	10	13	3	33.4	35.8	13	9	2	37.4	-38.4
6	13	3	16.6	9.0	8	13	3	20.4	17.9	10	14	0	40.9	-46.2	13	9	6	35.5	-34.4
6	13	7	11.8	15.9	8	14	0	23.7	-17.1	11	1	2	20.5	-12.1	13	10	1	26.4	-24.2
6	14	0	33.4	29.0	8	14	2	31.2	34.0	11	1	6	40.9	38.9	13	10	3	29.0	17.1
6	14	2	23.6	27.2	8	15	1	26.4	18.5	11	2	1	26.4	23.1	13	10	5	44.2	-41.8
6	15	1	16.6	9.6	8	16	0	29.0	26.6	11	2	7	23.7	-20.8	13	11	2	29.0	26.9
6	16	2	16.7	-11.0	8	18	0	40.9	-39.2	11	3	2	29.0	28.4	13	11	6	31.2	36.3
6	17	1	23.7	-28.0	8	19	1	20.4	18.6	11	3	4	31.2	28.6	13	12	3	20.5	-14.2
6	18	0	55.5	-52.7	8	20	0	29.0	24.6	11	3	6	33.4	34.7	13	12	5	20.4	16.1
6	19	1	33.4	34.2	9	1	2	89.2	83.1	11	4	5	35.4	36.0	13	15	6	16.7	-14.5
6	20	0	52.8	51.4	9	1	6	40.9	43.1	11	4	7	26.4	-24.9	13	16	1	20.5	-23.3
6	21	1	16.7	-17.3	9	2	1	67.8	70.0	11	5	2	23.7	-24.1	13	16	5	16.7	-16.0
6	22	0	16.7	-23.5	9	2	3	31.2	-33.1	11	5	4	11.8	6.7	13	17	2	20.4	15.9
7	1	2	26.4	18.5	9	2	5	31.2	30.4	11	5	6	61.5	-59.5	14	2	0	47.3	24.6
7	1	4	51.6	-40.5	9	2	7	16.7	-17.2	11	5	10	23.7	-23.6	14	4	0	23.6	26.4
7	1	6	37.4	34.5	9	3	2	11.8	14.2	11	6	1	82.0	-93.4	14	4	2	26.4	-25.6
7	1	8	16.7	-17.0	9	3	4	56.6	40.8	11	6	5	23.7	-21.8	14	4	4	23.6	18.2
7	2	1	33.4	29.3	9	3	8	16.6	13.2	11	6	7	37.4	32.3	14	5	1	60.3	-59.1
7	2	3	78.4	-74.2	9	4	1	39.2	37.3	11	7	6	51.5	48.4	14	5	5	35.5	-38.6
7	2	5	16.6	19.9	9	4	3	16.6	14.4	11	7	10	26.4	25.0	14	5	7	20.5	-17.2
7	3	2	67.0	-67.6	9	4	5	16.6	10.0	11	8	1	73.8	80.6	14	6	0	62.6	-70.1
7	3	4	23.7	-17.4	9	4	7	11.8	21.5	11	8	3	11.8	9.6	14	6	4	33.5	-35.4
7	3	6	31.2	-27.8	9	5	2	58.0	-51.1	11	8	5	26.4	24.2	14	7	1	51.5	60.5
7	4	1	81.9	87.4	9	5	4	11.8	-11.4	11	8	7	26.4	-28.6	14	7	3	16.6	3.0
7	4	3	11.8	-13.9	9	5	6	26.4	-19.5	11	9	2	40.9	-40.1	14	7	5	37.4	32.6
7	4	5	11.8	-6.3	9	5	8	29.0	-29.7	11	9	6	35.5	-36.0	14	7	7	23.6	16.4
7	4	7	29.0	29.5	9	6	1	40.9	-43.7	11	10	1	31.2	-28.2	14	8	0	100.2	113.8
7	4	9	35.5	-30.2	9	6	3	11.8	-15.2	11	10	5	42.6	-45.4	14	8	4	45.7	47.4
7	5	2	50.1	45.3	9	6	5	29.0	-26.3	11	11	6	26.4	25.4	14	9	1	26.4	-29.6
7	5	4	16.7	-20.2	9	6	7	16.6	13.8	11	11	8	20.5	-19.5	14	9	5	33.5	-29.7
7	5	6	20.4	13.9	9	7	2	51.5	48.3	11	12	3	16.6	7.8	14	9	7	16.7	-14.2
7	6	1	20.4	15.6	9	7	4	31.2	29.8	11	13	4	20.4	15.0	14	10	0	29.0	-29.3
7	6	3	16.7	-13.1	9	7	6	44.2	39.2	12	1	1	62.5	66.6	14	10	4	29.0	-26.6
7	6	5	11.8	11.4	9	7	8	20.4	20.6	12	1	5	20.4	13.1	15	4	1	23.6	20.8
7	6	7	16.7	-20.1	9	8	1	11.8	18.6	12	1	7	33.4	25.9	15	4	5	26.4	28.7
7	7	4	48.7	43.6	9	8	3	29.0	-29.4	12	2	0	23.6	19.2	15	5	2	29.0	-20.5
7	7	8	23.6	22.0	9	8	5	37.4	35.3	12	2	4	23.6	16.2	15	5	6	35.5	-32.8
7	8	1	31.2	-27.6	9	8	7	23.7	-20.3	12	3	1	11.8	12.6	15	6	1	20.5	-28.1
7	8	3	11.8	1.5	9	9	2	11.8	-14.7	12	3	3	11.8	11.2	15	6	5	33.5	-37.1
7	8	5	16.7	-11.9	9	9	4	11.8	6.6	12	3	5	16.6	8.7	15	7	2	26.4	29.5
7	9	2	31.2	-23.5	9	9	6	59.2	-54.5	12	3	7	23.6	14.8	15	7	6	39.2	32.3
7	10	1	23.6	22.8	9	10	1	11.8	-11.9	12	4	0	23.7	0.2	15	8	1	39.2	36.8
7	10	3	20.4	15.6	9	10	3	16.6	11.6	12	4	2	16.6	19.0	15	9	6	20.5	-27.2
7	10	5	26.4	22.0	9	10	5	27.4	-24.5	12	4	4	11.8	8.7	15	10	1	35.5	-36.6
7	12	1	40.9	-37.4	9	10	7	11.8	16.0	12	5	1	48.7	-44.2	15	1	3	35.4	38.3
7	12	3	48.7	-46.5	9	11	2	23.6	23.5	12	5	3	26.4	25.3	16	2	0	58.0	-51.4
7	12	5	20.5	-16.0	9	11	4	11.8	-15.1	12	5	5	35.5	-35.4	16	4	0	47.3	50.4
7	13	2	23.6	10.3	9	11	8	27.4	-22.2	12	5	7	33.5	-28.0	16	6	2	11.8	-25.2
7	13	6	16.6	7.7	9	12	3	11.8	13.7	12	6	0	125.1	-147.7	16	6	4	29.0	-28.7
7	14	1	26.4	23.4	9	13	4	16.6	16.5	12	6	4	44.2	-42.9	16	7	1	23.6	19.4
7	14	3	16.6	12.6	9	13	6	20.4	19.1	12	6	8	20.4	19.0	16	7	5	23.6	21.9
7	15	2	26.4	20.5	9	15	2	27.4	-27.2	12	7	1	52.8	60.8	16	8	0	52.8	51.7
7	16	1	20.4	9.5	9	15	4	27.4	-25.2	12	7	3	29.0	-27.8	16	9	1	16.7	-8.4
7	16	3	20.5	-5.5	9	17	4	16.6	15.2	12	7	5	33.4	31.9	16	9	5	16.7	-13.7
7	17	6	26.4	-19.0	10	1	1	47.3	44.7	12	7	7	40.9	36.1	16	9	7	11.8	-11.7
7	18	1	26.4	-19.1	10	1	3	29.0	-22.2	12	8	0	100.2	119.4	16	10	0	37.4	-41.3
7	18	5	16.7	-14.5	10	1	5	29.0	27.2	12	8	2	26.4	-25.6	17	1	2	44.2	39.8
7	19	6	23.6	19.1	10	2	0	80.2	82.2	12	8	4	57.9	58.0	17	5	2	29.0	-23.6
7	20	1	26.4	25.7	10	2	2	11.8	6.2	12	8	8	23.7	-20.3	17	6	5	11.8	-20.6
7	20	5	26.4	19.2	10	2	4	16.6	14.3	12	9	1	63.6	-68.0	17	7	2	26.4	22.2
8	1	1	23.7	-21.8	10	2	6	20.4	-13.6	12	9	5	47.3	-46.4	18	4	0	29.0	-21.7
8	1	3	52.9	-50.8	10	3	1	59.1	67.2	12	9	7	16.7	-16.1	18	6	0	29.0	22.3
8	1	5	44.2	35.8	10	3	3	29.0	25.4	12	10	0	33.5	-36.4	18	7	5	16.6	17.7
8	2	0	23.6	13.2	10	3	5	16.6	15.6	12	10	4	35.5	-34.3	19	4	1	26.4	-27.0
8	2	2	58.0	-55.4	10	4	0	23.7	-15.2	12	11	1	16.6	21.3	19	6	1	16.6	16.7
8	2	4	71.9	66.4															

DISCUSSION

The Disorder

The least squares refinement indicates a 15% interchange of Al and N atoms. There are two reasons why the method of estimating the amount of disorder could lead to a slightly low result. Firstly, the heavier atom might in fact be expected to have slightly lower temperature factors, and an increase in the amount of interchange would be required to achieve this result. Secondly, the scattering curves used were those for the neutral atoms, and since these atoms are four-covalent they might be expected to carry small charges, tending towards the formal charges of Al^- and N^+. This would also lead to an underestimate of the amount of interchange. Both of these effects should be small, however, and since the assumption of 15% interchange produced slight shifts of the temperature factors in the opposite direction to those originally obtained, it is probably very near the true value. The substantial difference between the Al-C and N-C bond lengths is not consistent with a greater amount of disorder.

The Packing

A projection of the structure down the C-axis is shown in Figure 1. Each molecule makes contacts with ten others. These neighbouring molecules are listed in Table 4. The co-ordinates are those of the centre

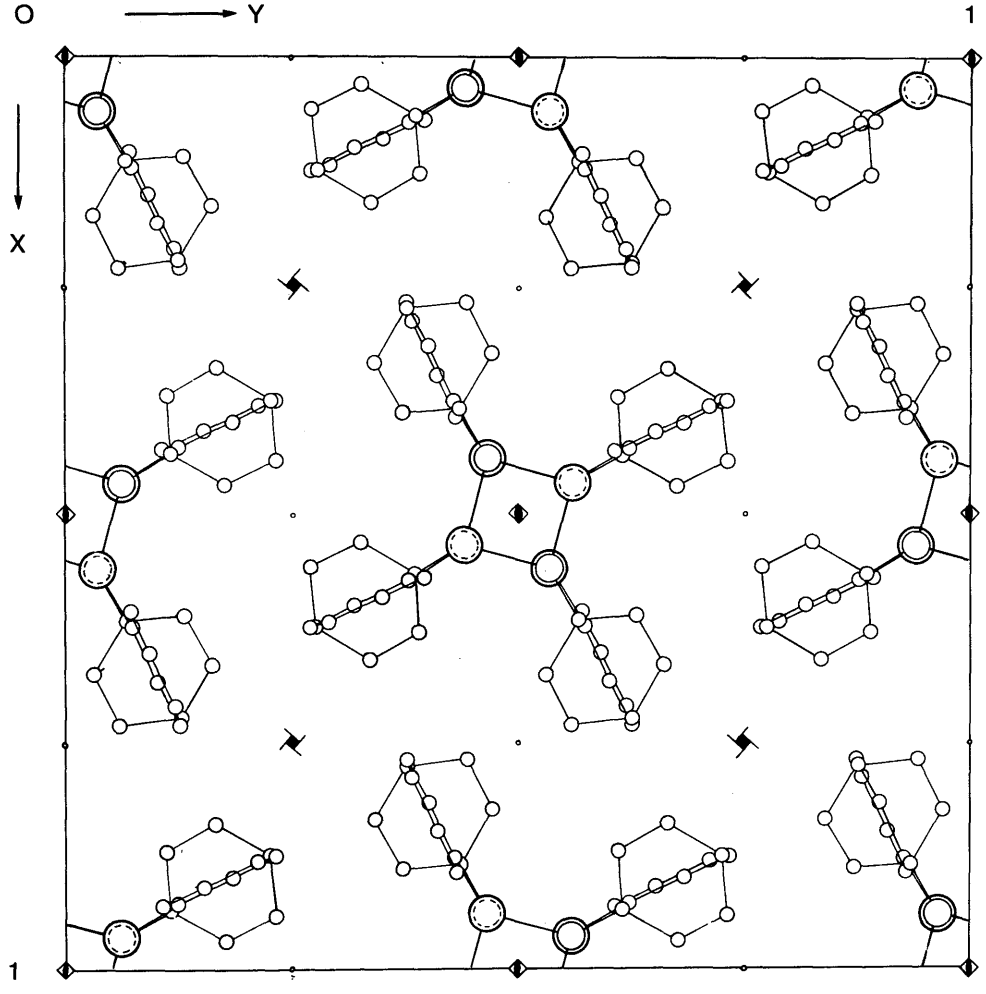


Figure 1.

c-axis projection of the contents of one unit cell (origin at $\bar{4}$).

of each molecule at $\bar{4}$, and the intermolecular distances are those between these centres.

Table 4

Neighbours of the Molecule at (0,0,0)

Number of contacts and distance	Co-ordinates of neighbours
4 at 10·33 Å	$(\pm 1/2, 0, -1/4), (0, \pm 1/2, 1/4)$.
2 at 10·82 Å	$(0, 0, \pm 1)$
4 at 12·85 Å	$(\pm 1/2, 0, 3/4)$, $(0, \pm 1/2, -3/4)$.

Hydrogen positions were calculated by assuming a C-H bond length of 1·0 Å, and these were used for the calculation of intermolecular contacts.

The two neighbours at 10·90 Å are related by the lattice translation in the z direction. Each of these molecules makes four symmetry related contacts of length 2·57 Å between H(4) of one molecule and H(10) of the neighbouring molecule.

The four neighbours at 10·36 Å are each related to the reference molecule by a centre of symmetry, and intermolecular contacts occur in pairs. H(11) of one molecule fits between the two phenyl groups of its neighbours and vice versa, to give contacts H(6)-H(11) of 2·69 Å. In addition H(5) of one molecule

approaches to 2·78 Å and 2·93 Å of C(11) and C(12) respectively of each adjacent molecule.

The four molecules at 12·92 Å are also related by centres of symmetry to the reference molecule. H(10) of one molecule contacts the three atoms C(3), C(4) and H(4) of the next molecule with distances of 2·97, 2·80, and 2·86 Å respectively.

There are no contacts of less than 3 Å with other molecules, and each molecule therefore makes a total of 56 contacts with its neighbours.

Molecular Dimensions

Figure 2 shows a projection down the a-axis.
The bond lengths and angles, (together with their estimated standard deviations) are given in Table 5.

The Al-N bond lengths are probably not affected by the disorder, since the regular cube shape of the molecule permits interchange of the Al and N atoms without any change in their co-ordinates. The three independent bond lengths observed are 1·904, 1·906, and 1·932 Å. These have standard deviations of 0·01 Å obtained from the least squares refinement, but an increase in these values is needed to allow for the rather large uncertainties in the cell dimensions. The first two values are dependent solely on the a lattice dimension and the third solely on the c dimension

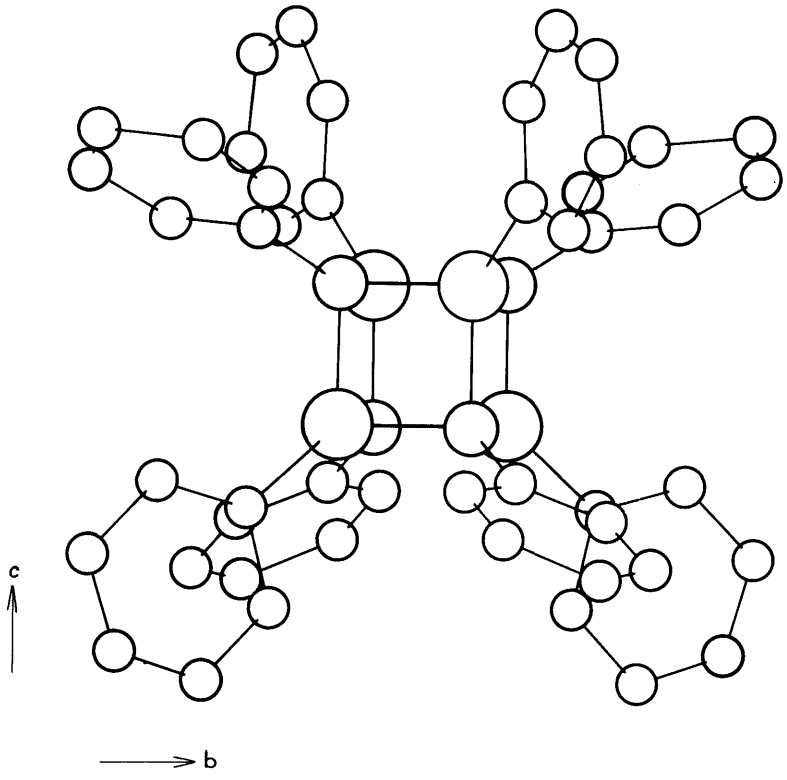


Figure 2.
a-axis projection of one molecule.

TABLE 5 MOLECULAR DIMENSIONS (E.S.D.s are given in brackets)

BOND			ANGSTROMS
Al	-	N	1.932(0.009)
Al	-	N*	1.906(0.009)
Al	-	N**	1.904(0.009)
Al	-	C(1)	1.859(0.015)
N	-	C(7)	1.470(0.015)
C(1)	-	C(2)	1.398(0.021)
C(2)	-	C(3)	1.415(0.026)
C(3)	-	C(4)	1.364(0.027)
C(4)	-	C(5)	1.382(0.026)
C(5)	-	C(6)	1.460(0.025)
C(6)	-	C(1)	1.389(0.021)
C(7)	-	C(8)	1.409(0.019)
C(8)	-	C(9)	1.390(0.023)
C(9)	-	C(10)	1.442(0.025)
C(10)	-	C(11)	1.413(0.023)
C(11)	-	C(12)	1.416(0.022)
C(12)	-	C(7)	1.378(0.019)

ANGLE				DEGREES
Al	-	N	- Al*	89.6(0.4)
Al	-	N	- Al**	89.7(0.4)
Al*	-	N	- Al**	90.0(0.4)
N	-	Al	- N*	90.4(0.4)
N	-	Al	- N**	90.3(0.4)
N*	-	Al	- N**	90.0(0.4)
N	-	Al	- C(1)	128.6(0.5)
N*	-	Al	- C(1)	123.2(0.5)
N**	-	Al	- C(1)	123.4(0.5)
Al	-	N	- C(7)	120.6(0.7)
Al*	-	N	- C(7)	128.8(0.7)
Al**	-	N	- C(7)	126.6(0.7)
Al	-	C(1)	- C(2)	115.6(1.1)
Al	-	C(1)	- C(6)	126.1(1.1)
N	-	C(7)	- C(8)	119.0(1.1)
N	-	C(7)	- C(12)	120.7(1.1)
C(1)	-	C(2)	- C(3)	121.0(1.6)
C(2)	-	C(3)	- C(4)	119.1(1.7)
C(3)	-	C(4)	- C(5)	123.6(1.7)
C(4)	-	C(5)	- C(6)	116.2(1.6)
C(5)	-	C(6)	- C(1)	121.7(1.5)
C(6)	-	C(1)	- C(2)	118.3(1.4)
C(7)	-	C(8)	- C(9)	121.7(1.4)
C(8)	-	C(9)	- C(10)	118.4(1.5)
C(9)	-	C(10)	- C(11)	119.6(1.5)
C(10)	-	C(11)	- C(12)	119.9(1.5)
C(11)	-	C(12)	- C(7)	120.3(1.4)
C(12)	-	C(7)	- C(8)	120.1(1.2)

Taking account of this their difference cannot be regarded as significant. These lengths may be compared with those found in aluminium nitride, where both Al and N are also four covalent. The lengths found there (Jeffrey, Parry, and Mozzi, 1956) are three of 1·885 Å and one of 1·917 Å. Bond lengths of 2.18 Å and 2·19 Å were found in $AlH_3 \cdot 2NMe_3$ (Heitsch, Nordman and Parry, 1963) and $AlH_3 \cdot Me_2NC_2H_4NMe_2$ (Palenik, 1964) respectively, but in these structures the aluminium is five co-ordinate. None of the inter-bond angles of the cube is significantly different from 90°.

All other bond lengths within the molecule involve the co-ordinates of carbon atoms, which are of low accuracy because of the positional disorder of these atoms. The Al-C and N-C bond lengths found are 1·87 Å and 1·47 Å. The maximum of the peak given by a disordered atom will lie between the two true positions. Assuming that this maximum is simply at the "centre of gravity" of the two positions, the Al-C and N-C distances should be corrected by an amount (1·86 - 1·47) x 0·15/ 0·70 = 0·08 Å. This gives Al-C and N-C distances of 1·94 Å and 1·39 Å respectively. The Al-C bond length is comparable with the 1·98 Å found in Al_2Me_6 (Vranka and Amma, 1964) and the 1·93 found in $(MeAlCl_2)_2$

(Allegra, Perego, and Immirzi, 1963).

The N-C length of 1·39 Å is rather short, however. If genuine it could be attributed to the increased amount of s character in this bond owing to the unusual angles of the other three bonds at the nitrogen atom.

The mean C-C bond length is 1·40 Å, with a rather large spread in the individual values. The standard deviations of the C-C bond lengths are high, however, and none of the differences from the mean is significant.

<u>The orientation of the phenyl groups</u>

The equations of the mean planes of the phenyl groups are:-

$C_1 - C_6$ (0·9038 X + 0·4263 Y + 0·0365 Z = 2·3565)

$C_7 - C_{12}$ (0·3876 X - 0·3134 Y - 0·8669 Z = -3·0086)

The dihedral angle between these planes is 79·3°. The aluminium atom is 0·097 Å from the plane of C(1) - C(6) and the nitrogen is 0·060 Å from the plane of C(7) - C(12). The greatest deviation of a carbon atom from the mean plane of its benzene ring is 0·012 Å.

<u>Relationship to the structure of Octaphenylcyclooctatetraene</u>

Freedman and Petersen (1962) published unit cell and space group data on a compound which they believed to be octaphenyl cubane, $C_8(C_6H_5)_8$, having a cube structure analogous to that found in this work. The publication

of preliminary results on $Al_4N_4(C_6H_5)_8$ by Jones and McDonald (1962) showed that the two compounds had the same space group and similar cell dimensions:-

$Al_4N_4(C_6H_5)_8$ (This work)	a = 19·93, c = 10·82 Å
$C_8(C_6H_5)_8$ (Freedman and Petersen)	a = 19·49, c = 10·65 Å

Because of this similarity it was assumed (Jones and McDonald, 1962, Throndsen and Zeiss, 1964) that the carbon compound had the structure found in this work for the Al-N compound (McDonald and McDonald, 1963). However, subsequent X-ray analysis of the carbon compound by Throndsen, Wheatley, and Zeiss, (1964) and by Pawley and Lipscombe, (1964), showed that the carbon compound is in fact octaphenylcyclooctatetraene.

The full results of Wheatley (1965) permit a comparison of the two structures, and a discussion of their apparent isomorphism. In Table 6 Wheatley's co-ordinates, after a transformation of axes, are compared with those of $Al_4N_4(C_6H_5)_8$. The positions of the outer carbon atoms in the two structures are quite similar, but those of the inner atoms are rather different. This difference was not great enough, however, to prevent Pawley and Lipscombe from arriving at the correct structure by least squares refinement, starting from a trial model which assumed a cube shape for the molecule.

TABLE 6

COMPARISON WITH OCTAPHENYLCYCLOOCTATETRAENE

ATOM	x	y	z
Al	0.0342	0.1917	0.0362
C(1)	0.0634	0.2025	0.0719
N	0.0341	0.1917	0.2148
C(8)	0.0199	0.1712	0.1730
C(1)	0.0713	0.1289	-0.0708
C(2)	0.0839	0.1554	-0.0341
C(2)	0.0675	0.1447	-0.1965
C(3)	0.0701	0.1769	-0.1588
C(3)	0.0899	0.0990	-0.2876
C(4)	0.0851	0.1304	-0.2596
C(4)	0.1177	0.0396	-0.2515
C(5)	0.1136	0.0658	-0.2359
C(5)	0.1243	0.0204	-0.1294
C(6)	0.1279	0.0451	-0.1129
C(6)	0.0995	0.0678	-0.0373
C(7)	0.1130	0.0897	-0.0101
C(7)	0.0648	0.1362	0.2841
C(9)	0.0549	0.1234	0.2617
C(8)	0.0297	0.0752	0.2949
C(10)	0.0257	0.0582	0.2881
C(9)	0.0574	0.0199	0.3543
C(11)	0.0608	0.0135	0.3698
C(10)	0.1238	0.0262	0.4062
C(12)	0.1250	0.0321	0.4214
C(11)	0.1591	0.0823	0.3932
C(13)	0.1546	0.0957	0.3941
C(12)	0.1287	0.1421	0.3318
C(14)	0.1187	0.1424	0.3125

The two structures are shown superimposed in Figure 3. The similarity in the outer parts of the two molecules is readily seen, and since it is this that determines the molecular packing, the two compounds have similar crystal structures.

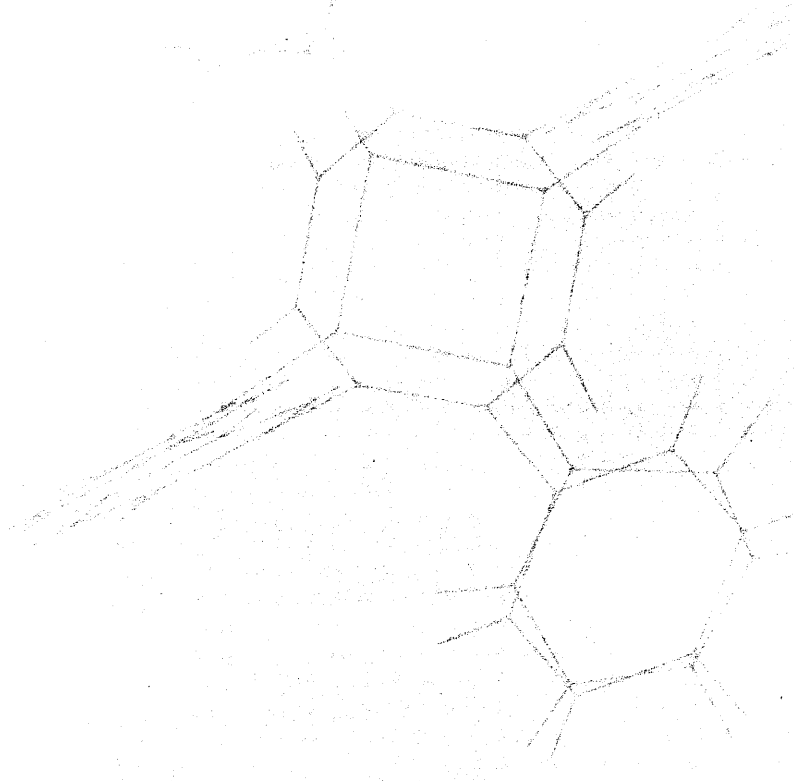


Figure 3.
Comparison with octaphenylcyclooctatetraene:
open circles - carbon compound
solid circles - Al-N compound

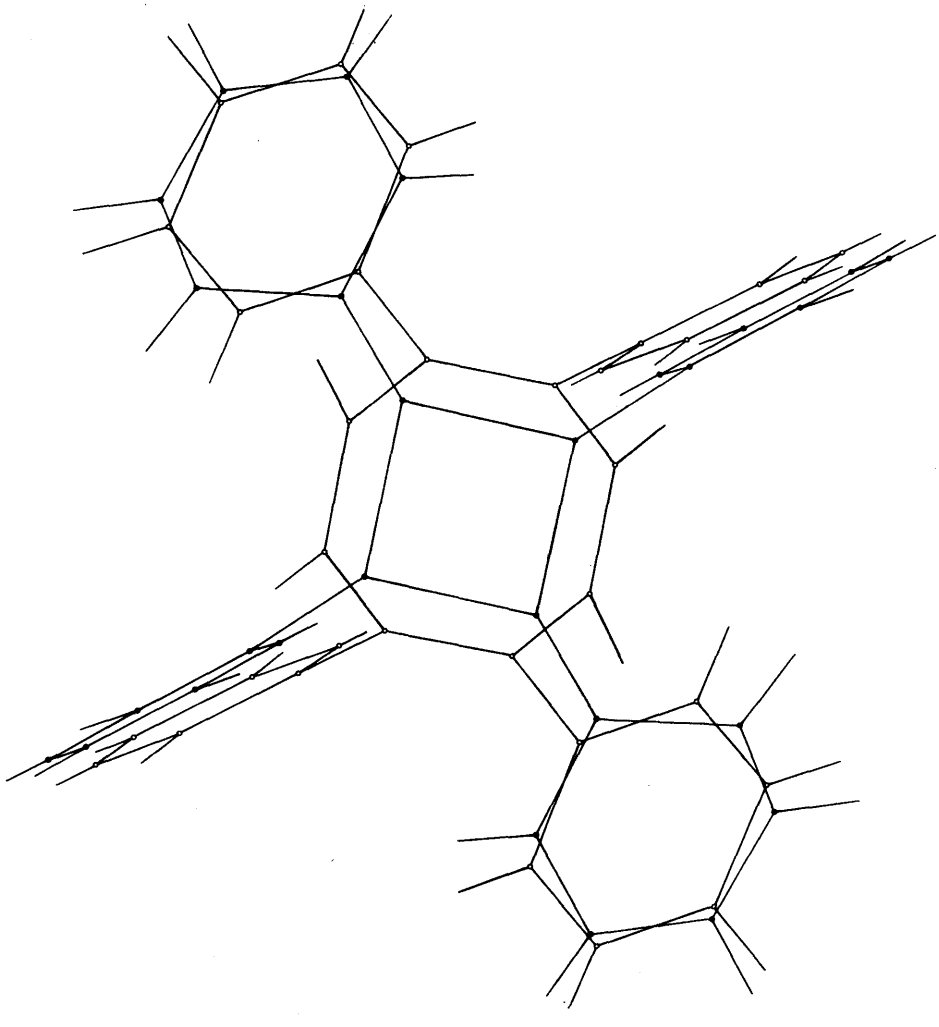


Figure 3.

Comparison with octaphenylcyclooctatetraene.

open circles - carbon compound
solid circles - Al-N compound

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CHAPTER 3

REFINEMENT OF THE STRUCTURE OF SODIUM METASILICATE

Introduction

Grund and Pizy (1952) determined the crystal structure of sodium metasilicate. Their analysis used partial 3-dimensional data, which was obtained photographically and gave an R value of 27%. They showed that the structure consists of infinite chains of silicate tetrahedra, with the chains linked together by co-ordination to sodium. The silicon oxygen bond lengths were found to be 1·57 and 1·67 Å, an unusually large difference for silicate structures. This refinement was undertaken in order to determine accurately the silicon-oxygen bond lengths and angles, which are relevant to the discussion of π-bonding in second row elements (Cruickshank, 1961).

Crystal Data

Na_2SiO_3, M = 122·07, Orthorhombic, a = 10·48, b = 6·07, c = 4·82 Å, U = 306·6 Å^3, Z = 4, D_c = 2·64. F_{ooo} = 240. Space group $Cmc2_1$ (No. 36). μ for MoKα radiation = 8·5 cm^{-1}.

Data collection

Crystals of Na_2SiO_3 were kindly supplied by Dr. F. Liebau. They were prepared by fusion of

equi-molar quantities of SiO_2 and Na_2CO_3 at 1100° and slow cooling of the melt. For the collection of the data an approximately equi-dimensional crystal of mean diameter about 0·3 mm (μR = 0·13) was selected and sealed in a Lindemann glass capillary.

Cell dimensions were reported by Grund and Pizy (1952), and by Seeman (1956). For this work they were remeasured from precession photographs, and on the linear diffractometer. The various measurements are given in Table 1.

Table 1

Determination	a, Å	b, Å	c, Å
Grund and Pizy	10·43	6·02	4·81
Seeman	10·52	6·075	4·825
Precession Photography	10·484	6·070	4·813
Diffractometer	10·482	6·064	4·826

Three-dimensional data were collected on the linear diffractometer (Arndt and Phillips, 1961), using MoKα radiation, balanced Strontium and Zirconium filters, and a scintillation counter with pulse height discrimination. The intensities were corrected for Lorentz and polarisation factors using programs written by J.G. Sime for the KDF9 computer. A small number of reflections observed at values not significantly above background were included at their observed values, this providing a simple means of treating "unobserved"

reflections. Subsequent examination of the discrepancies between F_o and F_c indicated that this procedure was justified. In this way a set of 315 independent structure amplitudes was obtained.

Least-squares refinement

The structure-factor least-squares program written by J.G.F. Smith and D.W.J. Cruickshank for the KDF9 computer was used. The starting point for the refinement was the set of co-ordinates obtained by Grund and Pizy, with isotropic temperature factors of U = 0·01 $\AA^2$ for all atoms. The form factors for the neutral atoms given in volume three of International Tables for X-ray crystallography were used. An initial structure factor calculation gave a residual ($R = \sum|k\ F_o - |F_c|| / \sum kF_o$) of 0·196. Two cycles of full matrix refinement of the co-ordinates, individual isotropic temperature factors, and the overall scale factor were carried out, using the weighting scheme $w = 1$ for $F_o \leqslant 6$, $w = 36/F_o^2$ for $F_o > 6$. This reduced the residual to 0·050. At this point an analysis of the discrepancies between F_o and F_c showed that this weighting scheme was inadequate. There was a slight decrease in the accuracy of the data with increasing F_o, and a sharp decrease in accuracy at very low sine theta values, probably arising from setting errors in the diffractometer at low angles.

A few very strong reflections seemed to be affected by extinction, and required down-weighting. The weighting scheme was changed to $w = [1 - \exp(-4(\sin\theta/\lambda)^2)]/(20 + F_o + 0{\cdot}02\,F_o^2)$ and two further cycles of refinement were carried out, reducing the residual to 0·045, with a considerable improvement in the standard deviations.

At this point the isotropic refinement had converged, and anisotropic refinement was begun. One cycle produced a highly significant degree of refinement, and reduced the residual to 0·032. A second cycle produced no significant shifts. The effect of anisotropic refinement, however, was to produce a great improvement in the agreement of F_o and F_c for high order reflections, and a further change in the weighting scheme was indicated. ($w = [1 - \exp(-0{\cdot}5(\sin\theta/\lambda)^2]/(1+0{\cdot}0001\,F_o^3)$) was found to be more suitable, and two further cycles were carried out using this weighting scheme. No further reduction in the residual was obtained, but R' ($= \sum w(|F_o| - |F_c|)^2/\sum w F_o^2$) and the standard deviations were appreciably reduced.

Two additional cycles were carried out, using the form factors for Na^+ instead of those for the neutral atom. These produced no significant change in the parameters or residual.

The final co-ordinates and standard deviations are

given in Table 2, and the temperature factors and their standard deviations in Table 3. The estimated standard deviations are those given by inversion of the full least-squares matrix. Observed and calculated structure factors are given in Table 4.

Discussion of the structure

a. General Description.

Projections of the structure down [001] and [010] are shown in Figures 1 and 2. The metasilicate chains are parallel to the c-axis, and have $mc2_1$ symmetry with two tetrahedra in the repeat unit. The silicon and the bridging oxygen lie in the mirror plane. The oxygens are further co-ordinated to sodium atoms, which link the chains together in the a and b directions. Li_2SiO_3 (Seeman, 1956), Na_2GeO_3 (Ginetti, 1954), and Li_2GeO_3 (Hahn and Theune, 1957) have been shown to have the same structure as sodium metasilicate.

b. Relationship to the Zincite structure.

Grund and Pizy (1952) noted that sodium metasilicate shows pseudo-hexagonal symmetry. The reason for the pseudo-symmetry may be seen by reference to Figure 3. This shows the tetrahedra of oxygen atoms around silicon and sodium projected down the c-axis, assuming tetrahedral co-ordination of the sodium. One layer

TABLE 2

FINAL FRACTIONAL CO-ORDINATES AND ESTIMATED STANDARD DEVIATIONS

ATOM	x	y	z
Na	0.16562(9)	0.33880(15)	0
Si	0	0.15737(11)	0.53676(32)
O(1)	0.12947(15)	0.28733(28)	0.48105(47)
O(2)	0	0.08436(37)	0.87224(58)

TABLE 3

TEMPERATURE FACTORS AND THEIR ESTIMATED STANDARD DEVIATIONS

ATOM	U11	U22	U33	2U23	2U31	2U12
Na	0.0117(4)	0.0120(4)	0.0163(7)	-0.0006(7)	-0.0011(4)	-0.0008(5)
Si	0.0057(3)	0.0045(3)	0.0087(3)	0.0005(5)	0	0
O(1)	0.0086(6)	0.0128(6)	0.0142(6)	0.0021(8)	0.0031(8)	-0.0059(11)
O(2)	0.0168(9)	0.0071(8)	0.0094(7)	0.0034(11)	0	0

TABLE 4

OBSERVED AND CALCULATED STRUCTURE FACTORS

H	K	L	Fo	Fc	H	K	L	Fo	Fc	H	K	L	Fo	Fc	H	K	L	Fo	Fc
2	0	0	35.3	36.5	3	5	1	59.2	62.1	10	2	3	15.3	15.3	7	1	5	8.2	8.8
4	0	0	21.6	18.3	5	5	1	15.5	15.3	12	2	3	32.1	32.2	9	1	5	21.9	22.2
6	0	0	92.4	105.5	7	5	1	6.2	5.9	1	3	3	13.9	14.0	11	1	5	12.2	12.7
8	0	0	41.9	42.5	9	5	1	35.1	35.4	3	3	3	24.5	25.3	13	1	5	8.5	8.6
10	0	0	9.6	9.6	11	5	1	14.3	13.7	5	3	3	16.3	15.9	0	2	5	28.7	29.3
12	0	0	33.4	33.5	0	6	1	27.2	26.7	7	3	3	10.7	10.3	2	2	5	11.6	11.6
14	0	0	16.4	16.9	2	6	1	4.4	4.3	9	3	3	9.0	8.9	4	2	5	9.8	9.7
3	1	0	81.7	88.4	4	6	1	9.6	9.1	11	3	3	11.6	11.7	6	2	5	25.4	25.9
5	1	0	27.7	25.2	6	6	1	12.6	12.3	13	3	3	6.6	6.3	8	2	5	11.3	11.7
7	1	0	10.1	9.0	8	6	1	14.6	14.1	0	4	3	22.2	21.8	10	2	5	7.7	7.9
9	1	0	36.9	36.3	1	7	1	6.9	6.9	2	4	3	6.9	6.9	12	2	5	17.5	17.9
11	1	0	10.7	14.0	3	7	1	26.2	26.5	4	4	3	7.6	7.8	1	3	5	1.6	1.4
13	1	0	9.5	9.1	5	7	1	5.2	5.3	6	4	3	24.5	24.7	3	3	5	13.4	13.5
0	2	0	75.2	77.8	7	7	1	5.1	5.4	8	4	3	12.5	12.5	5	3	5	8.8	8.7
2	2	0	13.7	12.1	0	8	1	42.3	42.6	10	4	3	4.0	4.3	7	3	5	2.5	2.5
4	2	0	42.2	40.4	2	8	1	11.2	11.1	12	4	3	21.2	20.9	9	3	5	2.6	2.7
6	2	0	29.8	30.3	2	0	2	7.7	3.5	1	5	3	12.4	12.6	11	3	5	7.8	7.9
8	2	0	15.9	16.1	4	0	2	31.0	30.4	3	5	3	38.3	39.4	0	4	5	21.2	21.1
10	2	0	5.6	5.0	6	0	2	66.0	72.2	5	5	3	10.2	10.4	2	4	5	15.5	15.2
12	2	0	2.8	3.3	8	0	2	25.5	24.9	7	5	3	10.7	10.6	4	4	5	9.6	9.8
14	2	0	4.7	4.9	10	0	2	4.1	3.6	9	5	3	23.8	24.1	6	4	5	17.4	17.4
1	3	0	11.5	10.5	12	0	2	24.2	24.1	11	5	3	8.8	8.7	8	4	5	17.6	17.1
3	3	0	90.3	100.0	14	0	2	10.7	10.7	0	6	3	19.7	19.4	10	4	5	9.6	9.5
5	3	0	19.8	18.8	1	1	2	10.5	8.7	2	6	3	5.1	5.1	12	4	5	13.4	13.1
7	3	0	4.1	3.7	3	1	2	50.9	51.1	4	6	3	10.6	10.3	1	5	5	17.2	17.3
9	3	0	43.9	44.2	5	1	2	10.1	8.5	6	6	3	9.6	9.6	3	5	5	23.4	23.3
11	3	0	16.9	16.7	7	1	2	2.7	2.2	8	6	3	10.7	10.7	5	5	5	13.1	12.9
13	3	0	9.9	9.8	9	1	2	24.6	23.9	1	7	3	3.7	3.9	7	5	5	15.0	14.8
0	4	0	41.0	41.0	11	1	2	7.4	6.9	3	7	3	15.5	15.9	9	5	5	16.5	16.7
2	4	0	15.3	15.1	13	1	2	4.4	3.9	5	7	3	3.5	3.9	0	6	5	11.1	11.2
4	4	0	25.0	25.4	0	2	2	66.0	66.1	0	8	3	25.8	26.2	2	6	5	4.3	4.4
6	4	0	40.6	40.3	2	2	2	15.1	14.1	2	0	4	23.3	23.9	4	6	5	9.5	9.5
8	4	0	3.7	3.3	4	2	2	30.3	29.2	4	0	4	34.7	36.3	6	6	5	7.2	6.0
10	4	0	12.0	11.5	6	2	2	31.2	31.5	6	0	4	36.2	37.1	8	6	5	6.2	6.3
12	4	0	28.2	28.5	8	2	2	17.2	17.4	8	0	4	12.4	12.0	1	7	5	8.2	8.1
1	5	0	22.6	21.7	10	2	2	7.5	7.2	10	0	4	15.4	15.6	3	7	5	11.1	10.7
3	5	0	22.2	21.5	12	2	2	8.8	8.9	12	0	4	17.5	17.9	2	0	6	19.9	21.5
5	5	0	1.1	2.3	1	3	2	18.7	17.8	1	1	4	17.1	17.2	4	0	6	27.1	27.8
7	5	0	14.4	15.9	3	3	2	73.6	80.5	3	1	4	21.9	21.3	6	0	6	23.6	24.3
9	5	0	1.9	0.4	5	3	2	17.9	17.3	5	1	4	10.2	10.1	8	0	6	11.8	11.7
11	5	0	5.4	5.1	7	3	2	13.1	12.6	7	1	4	12.5	12.6	10	0	6	15.5	15.4
0	6	0	38.2	38.1	9	3	2	38.0	38.3	9	1	4	12.9	12.8	12	0	6	16.9	16.8
2	6	0	1.8	0.9	11	3	2	15.5	15.0	11	1	4	5.9	6.1	1	1	6	13.4	14.4
6	6	0	31.6	31.9	13	3	2	9.0	9.3	13	1	4	5.1	5.2	3	1	6	15.7	16.0
1	7	0	10.2	10.6	0	4	2	29.5	28.6	0	2	4	36.5	37.0	5	1	6	11.2	11.0
3	7	0	15.5	15.0	2	4	2	7.2	6.8	2	2	4	8.2	7.7	7	1	6	12.0	11.8
5	7	0	3.0	2.6	4	4	2	15.7	15.1	4	2	4	16.0	15.5	9	1	6	11.9	11.7
7	7	0	10.0	10.5	6	4	2	30.4	29.6	6	2	4	21.2	21.0	11	1	6	7.6	7.4
0	8	0	10.2	10.2	8	4	2	5.2	5.0	8	2	4	12.0	12.0	13	1	6	6.4	6.2
1	1	1	35.2	33.0	10	4	2	7.4	7.1	10	2	4	5.6	5.4	0	2	6	13.4	13.4
3	1	1	45.7	49.4	12	4	2	22.5	22.5	12	2	4	8.4	8.4	2	2	6	4.5	4.5
5	1	1	26.9	24.9	1	5	2	16.6	16.3	1	3	4	21.8	21.2	4	2	6	11.5	11.5
7	1	1	20.6	21.0	3	5	2	26.3	26.2	3	3	4	45.2	45.9	6	2	6	7.5	7.4
9	1	1	51.4	53.5	5	5	2	10.7	10.5	5	3	4	15.0	14.4	8	2	6	3.8	3.6
11	1	1	9.8	9.8	7	5	2	13.3	12.8	7	3	4	17.5	17.0	10	2	6	4.7	4.5
13	1	1	5.8	5.4	9	5	2	8.9	9.0	9	3	4	25.8	25.8	12	2	6	5.2	5.6
0	2	1	61.3	63.9	11	5	2	8.8	8.8	11	3	4	11.0	11.0	1	3	6	18.0	17.8
2	2	1	23.4	21.5	0	6	2	41.9	42.5	0	4	4	19.3	19.1	3	3	6	21.5	21.2
4	2	1	19.1	18.2	2	6	2	17.3	17.2	2	4	4	11.6	11.0	5	3	6	10.7	10.5
6	2	1	58.6	58.6	4	6	2	16.0	16.0	4	4	4	8.3	8.0	7	3	6	15.4	15.2
8	2	1	13.7	13.1	6	6	2	34.6	35.3	6	4	4	17.6	17.2	9	3	6	15.2	14.9
10	2	1	9.9	9.3	8	6	2	13.2	13.4	8	4	4	12.5	12.5	11	3	6	7.4	7.1
12	2	1	35.6	35.9	1	7	2	16.6	16.8	10	4	4	6.5	6.7	0	4	6	15.5	15.6
14	2	1	6.6	6.9	3	7	2	20.7	21.4	1	5	4	6.4	6.4	2	4	6	11.4	11.1
1	3	1	32.5	30.7	5	7	2	11.8	11.9	3	5	4	20.5	20.6	4	4	6	8.0	7.7
3	3	1	20.6	20.0	0	8	2	6.7	6.9	5	5	4	9.4	9.3	6	4	6	12.5	12.4
5	3	1	10.7	10.0	2	8	2	1.4	2.3	7	5	4	5.9	6.0	8	4	6	12.6	12.2
7	3	1	18.7	18.8	1	1	3	26.4	25.7	9	5	4	7.7	7.6	10	4	6	7.3	7.0
9	3	1	7.7	7.6	3	1	3	47.2	48.9	0	6	4	31.1	31.4	1	5	6	5.5	5.4
11	3	1	7.9	8.0	5	1	3	22.7	22.7	2	6	4	13.1	13.5	3	5	6	3.7	8.4
13	3	1	3.5	3.4	7	1	3	19.6	20.3	4	6	4	12.3	12.4	5	5	6	3.8	3.9
0	4	1	43.4	43.5	9	1	3	41.8	42.4	6	6	4	26.2	26.6	7	5	6	5.4	5.5
2	4	1	13.1	12.6	11	1	3	14.9	14.5	8	6	4	11.2	11.3	9	5	6	2.1	1.5
4	4	1	27.6	27.4	13	1	3	10.5	10.3	1	7	4	12.6	12.7	0	6	6	11.7	11.7
6	4	1	45.1	46.1	0	2	3	60.5	62.4	3	7	4	17.4	17.3	2	6	6	5.9	6.2
8	4	1	1.5	1.5	2	2	3	25.8	25.6	5	7	4	9.8	10.2	4	6	6	4.9	5.1
10	4	1	10.0	9.9	4	2	3	24.9	25.0	1	1	5	9.3	9.9	6	6	6	10.4	10.0
12	4	1	33.6	33.5	6	2	3	50.9	52.5	3	1	5	25.4	25.6	1	7	6	2.0	2.1
1	5	1	7.4	7.3	8	2	3	19.3	19.0	5	1	5	16.0	16.2					

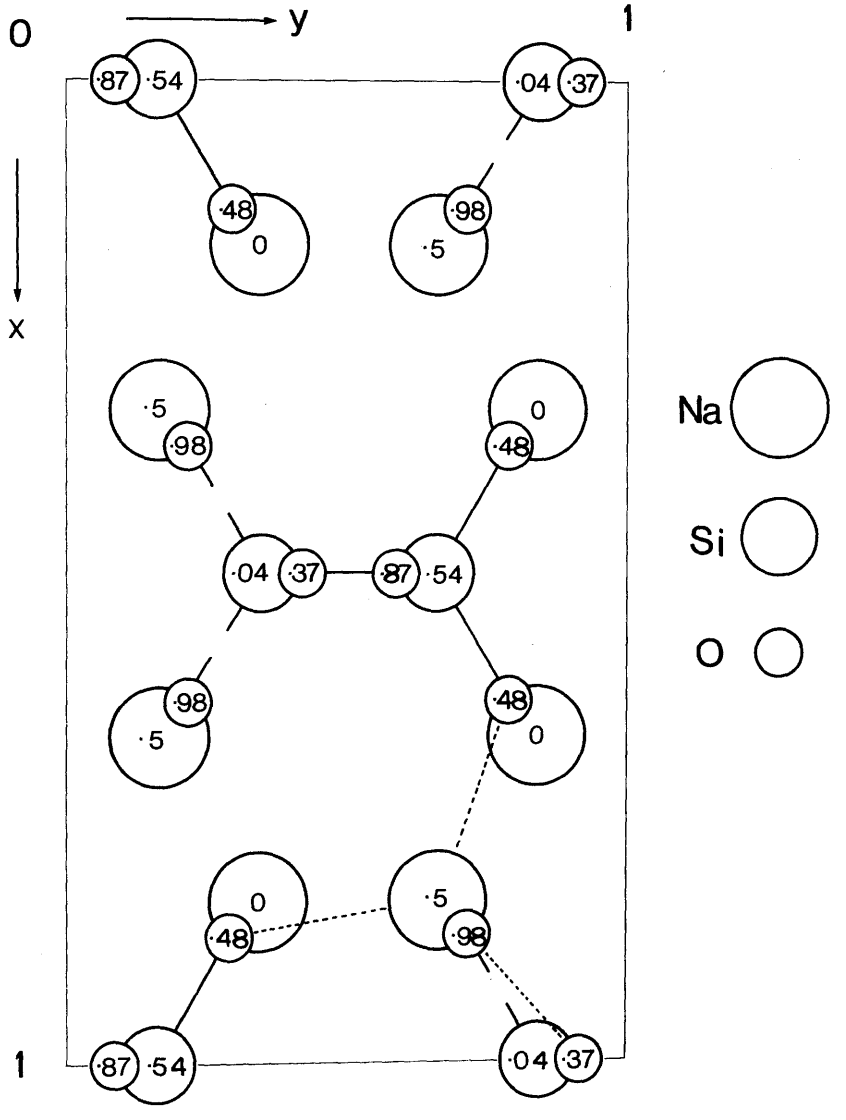

Figure 1.
Projection of the structure down the c-axis.

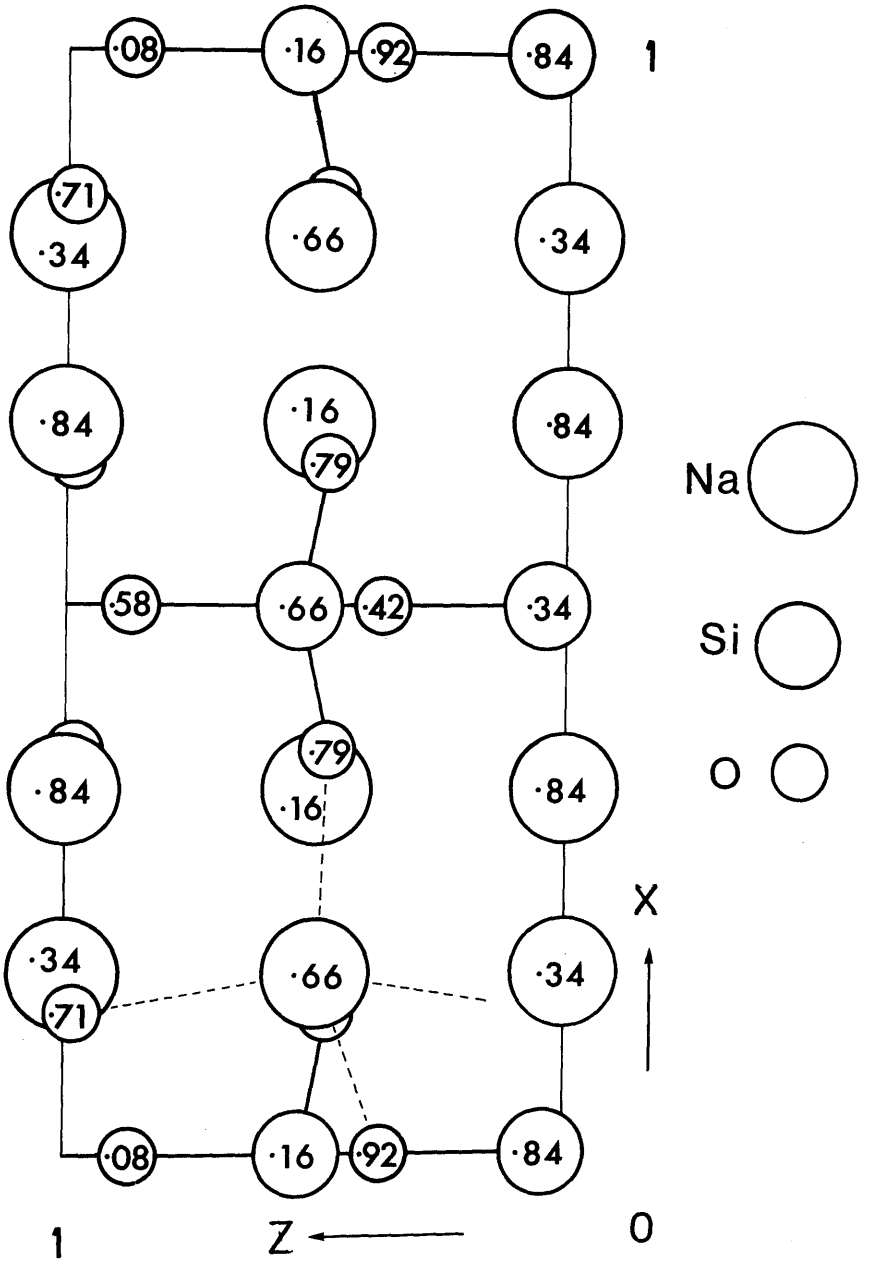

Figure 2.

Projection of the structure down the b-axis.

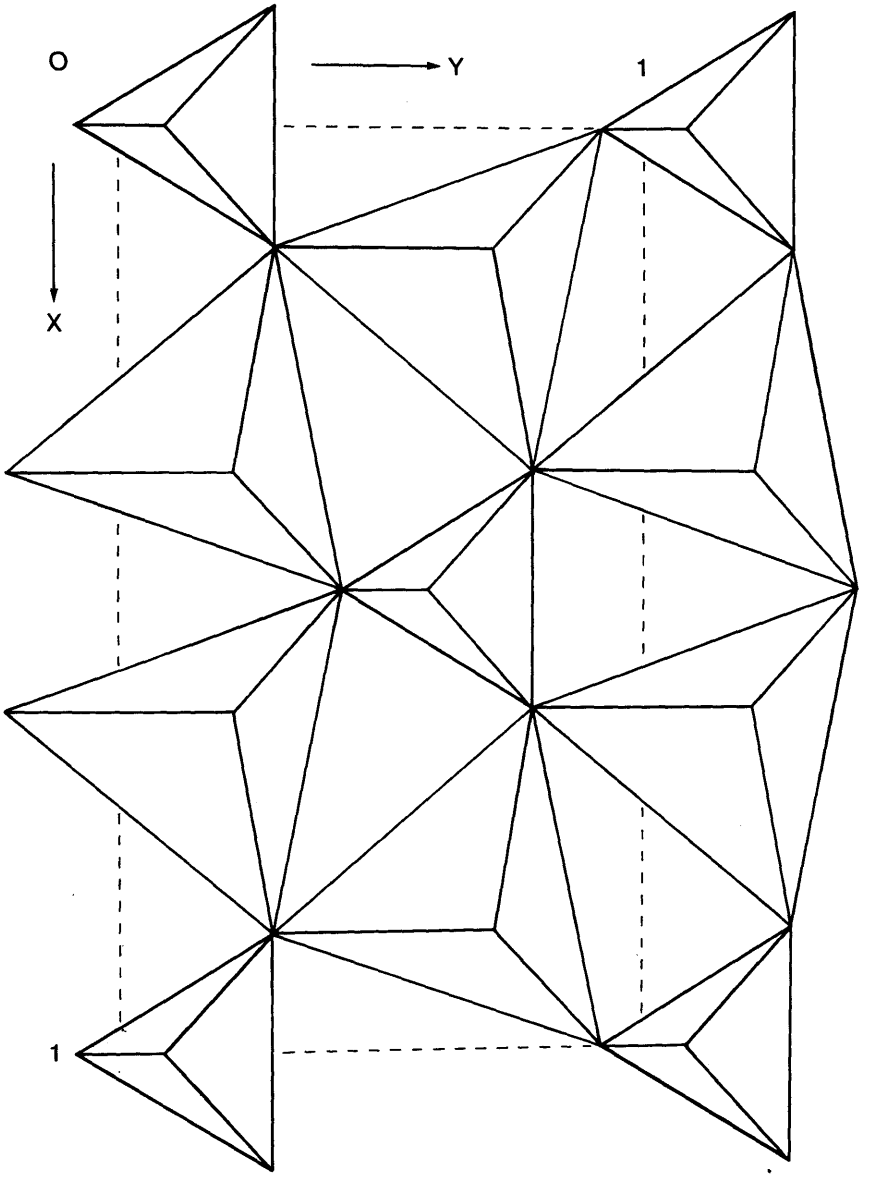

Figure 3.
Projection down the c-axis, showing the oxygen tetrahedra.

of the structure is shown. The repeat distance of the cell covers two such layers, related by the 2_1 axis. The pattern of tetrahedra is that found in the structure of zincite, ZnO, and is also known for other simple binary compounds. In sodium metasilicate we have two thirds of the zinc atoms replaced by sodium, and one third by silicon, destroying the hexagonal symmetry. They remain close to their hexagonal positions, however, and the oxygens are shifted because of the difference of about 0·7 Å between the silicon-oxygen and sodium-oxygen bond lengths. Because of the similar scattering powers of sodium and silicon the structure shows pseudo-hexagonal symmetry, particularly in the hk0 projection. The dimensions of the pseudo-hexagonal cell of sodium metasilicate are $a' = a/3 = 3{\cdot}49$ Å, $b' = b/\sqrt{3} = 3{\cdot}50$ Å, $c' = c = 4{\cdot}82$ Å, and the space group, $Cmc2_1$, is a sub-group of $P6_3mc$, the zincite space group, with the orthorhombic cell having six times the volume of the hexagonal one. Table 5 shows the fractional co-ordinates of the atoms in sodium metasilicate, together with the values they would be required to have in the hexagonal structure. The co-ordinates of the sodium and silicon are seen to correspond quite closely.

Table 5

Atom	Co-ords. found in Na_2SiO_3	Co-ords. for hexagonal structure
Na	0·166, 0·339, 0	0·166, 0·333, 0
O(1)	0·129, 0·287, 0·481	0·166, 0·333, z
Si	0, 0·157, 0·537	0 , 0·166, 1/2
O(2)	0, 0·084, 0·872	0, 0·166, z + 1/2

c. The Sodium Co-ordination.

The bond lengths and angles at sodium are given in Table 6. The estimated standard deviations are 0·002 Å for the bond lengths and 0·08° for the angles. As discussed in the previous section, the structure is related to the tetrahedral structure of zincite. Apart from the differences due to differing Si-O and Na-O bond distances, the main distortion is such as to increase the sodium co-ordination from four to five. The "extra" Na-O bond is that to O(1)***, with the longest distance of 2·55 Å. The polyhedron of five oxygens is a distorted trigonal bipyramid, with the largest distortions involving O(1)***.

d. The Metasilicate Chain.

The bond lengths and angles of the metasilicate chain are given in Table 6. The estimated standard deviations are 0·002 Å for the bond lengths and about 0·1° for the angles. The bridging Si-O bonds, of mean length 1·672 Å,

TABLE 6
BOND LENGTHS AND ANGLES

BOND			ANGSTROMS
Na	-	O(1)	2.370
Na	-	O(1)*	2.303
Na	-	O(1)**	2.282
Na	-	O(1)***	2.549
Na	-	O(2)	2.404
Si	-	O(1)	1.592
Si	-	O(2)	1.677
Si	-	O(2)*	1.668

ANGLE					DEGREES
O(1)	-	Na	-	O(1)*	98.19
O(1)	-	Na	-	O(1)**	98.36
O(1)	-	Na	-	O(1)***	156.94
O(1)	-	Na	-	O(2)	92.90
O(1)*	-	Na	-	O(1)**	118.95
O(1)*	-	Na	-	O(1)***	93.29
O(1)*	-	Na	-	O(2)	120.29
O(1)**	-	Na	-	O(1)***	93.41
O(1)**	-	Na	-	O(2)	116.99
O(2)	-	Na	-	O(1)***	64.06
O(1)	-	Si	-	O(1)*	116.89
O(1)	-	Si	-	O(2)	107.07
O(1)	-	Si	-	O(2)*	110.83
O(2)	-	Si	-	O(2)*	103.06
Si	-	O(2)	-	Si*	133.72
Si	-	O(2)	-	Na	94.43
Si*	-	O(2)	-	Na	116.33
Na	-	O(2)	-	Na*	92.46
Si	-	O(1)	-	Na	128.98
Si	-	O(1)	-	Na*	128.45
Si	-	O(1)	-	Na**	111.50
Si	-	O(1)	-	Na***	91.25
Na	-	O(1)	-	Na*	100.04
Na	-	O(1)	-	Na**	86.16
Na	-	O(1)	-	Na***	82.07
Na*	-	O(1)	-	Na**	83.26
Na*	-	O(1)	-	Na***	79.39
Na**	-	O(1)	-	Na***	156.94

and the non-bridging ones, of length 1·592 Å, show an unusually large difference. Cruickshank's (1961) discussion of bond lengths in terms of d-p π-bonding suggests that there should be a considerable difference between the lengths of bridging and non-bridging bonds. The fact that such differences are not normally observed in silicate structures may be attributed to the tendency of the silicate "ion" to shed its negative charge, and with this some of its π-bonding potential, by forming partial covalent bonds to the cations. In the case of sodium metasilicate, where we have a rather electro-positive cation, this tendency is minimised. Rather larger differences between bridging and non-bridging bond lengths should therefore be found. A number of other metasilicates have been subjected to accurate structure refinements recently. In Wollastonite, $CaSiO_3$ (Buerger and Prewitt, 1961). The bridging Si-O bonds have mean length 1·655 Å, and the non-bridging ones are of mean length 1·598 Å. In Bustamite, $CaMn(SiO_3)_2$ (Peacor and Buerger, 1962) they are 1·642 Å and 1·603 respectively, and in Rhodonite, (Peacor and Niizeki, 1963) $(Ca,Mn)SiO_3$, mean lengths of 1·648 Å and 1·608 Å were found. The structure of Stokesite,

$CaSnSi_3O_9 \cdot 2H_2O$ (Vorma, 1963) shows mean lengths of 1·630 Å and 1·616 Å for the bridging and non-bridging bonds. These smaller differences parallel the lower electropositive character of calcium, manganese and tin compared with sodium. Associated with the smaller difference in bond length is an increase in the angle at the bridging oxygens. The angle of 133·7° in sodium metasilicate should be compared to the mean values of 143°, 144°, 137° and 147° in the four calcium metasilicates mentioned above.

The distortions of the bond angles at silicon from the tetrahedral value may be attributable to the co-ordination requirements of the sodium, discussed in the previous section. They could also be attributed to slight changes in the s and p character of the orbitals used for silicon-oxygen bond formation. The O(2)-Si-O(2)* angle of 103° and the O(1)-Si-O(1)* angle of 117° suggest an increased s character in the shorter non-bridging bonds.

e. Oxygen co-ordination

The bond angles at oxygen are given in Table 6. O(2) is linked to two silicon atoms and to two sodiums. In order that the sodium may achieve a co-ordination of five, oxygen O(1) must also become five co-ordinate. It is linked to one silicon atom and to four sodiums. The arrangement is a highly distorted trigonal bipyramid.

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CHAPTER 4

REFINEMENT OF THE STRUCTURE OF HEMIMORPHITE

Hemimorphite is a zinc silicate mineral of empirical formula $Zn_2SiO_4.H_2O$. Ito and West (1932) studied the crystal structure and showed that it contained Si_2O_7 groups, and that the formula should be written $Zn_4Si_2O_7(OH)_2.H_2O$. These workers assumed that the Si_2O_7 grouping had a linear Si-O-Si linkage. A redetermination of the structure by Barclay and Cox (1960), using 2-dimensional data for two projections, indicated an Si-O-Si angle of 133°, and an unusually long Si-O bond of 1·72 Å. These results were not of great accuracy however, because of overlapping of the bridging oxygen in one of the projections. Because of the interest in d-p π-bonding in silicon-oxygen bonds, and the light thrown on the problem by the observed variations in these bond lengths and angles, (Cruickshank, 1961) a 3-dimensional refinement of the structure was carried out.

Crystal Data

Hemimorphite, $Zn_4Si_2O_7(OH)_2.H_2O$, M = 481·7. Orthorhombic, a = 8·370, b = 10·719, c = 5·120 Å, U = 459·4 Å^3, Z = 2, D_c = 3·482. F_{000} = 464. Space group Imm2 (No. 44).

Cell dimensions

These have been previously measured by Gossner and Mussgnug (1929), by Ito and West (1932), by Swanson and Fuyat (1953), and by Barclay and Cox (1960). In this work they were remeasured from zero-layer precession photographs, and on the Hilger linear diffractometer (Arndt and Phillips, 1961). The values obtained were in close agreement with those of Swanson and Fuyat, and their more accurate values were used in this analysis. The various determinations are listed in Table 1, with kX values converted to Å for the first two determinations.

Table 1

Determination	a, Å	b, Å	c, Å
Gossner and Mussgnug	8·43	10·75	5·15
Ito and West	8·40	10·72	5·12
Barclay and Cox	8·37	10·67	5·10
Swanson and Fuyat	8·370	10·719	5·120
Precession Data	8·369	10·728	5·116
Diffractometer	8·373	10·718	5·120

Initial refinement of photographic data

Three-dimensional data were obtained by visual estimation of equi-inclination Weissenberg photographs of reciprocal lattice layers hk0 to hk7, taken with MoKα radiation. The crystal used had dimensions of approximately 0·02 x 0·06 x 0·2 mm., with the longest dimension parallel to

the rotation axis, and therefore the effect of absorption could be neglected. Corrections for Lorentz and polarisation factors were applied using a Pegasus computer programme written by J.G.F. Smith. In addition, precession photographs of layers h0l to h2l and 0kl to 2kl were estimated, and corrections for Lorentz and polarisation factors applied graphically. The data were then put on a single scale by the layer scale correlation method of Rollett and Sparks, (1960) using a Pegasus programme written by J.G.F. Smith. This yielded a set of 568 independent structure amplitudes.

The starting point for the refinement was the set of parameters found by Barclay and Cox, and co-ordinates and anisotropic temperature factors were refined. The block diagonal least squares programme of J.S. Rollett (1961) for the Deuce computer was used. $\sum w(K|F_o| - |F_c|)^2$ was minimised, with $\sqrt{w} = 1$ for $K F_o \leq 23{\cdot}5$ and $\sqrt{w} = 23{\cdot}5/K F_o$ for $K F_o > 23{\cdot}5$. No allowance was made for the anomalous scattering of the zinc atoms.

Twelve cycles of refinement were needed to produce convergence, reducing the residual $R = \sum(K||F_o| - |F_c||)/\sum K|F_o|$, from an initial value of 0·137 to 0·087. In addition, one cycle was carried out using the co-ordinates of Barclay and Cox, but with the z co-ordinates of O(4)

and O(5) interchanged, in order to check on the ambiguity arising from the overlap of these two atoms in one of their projections. The shifts obtained in this cycle suggested that the two sets of starting parameters would converge to the same final structure.

It became apparent during the refinement that there were some rather large errors in the layer scale factors obtained from the correlation programme. In particular, there seemed to be an error of 10% or more in the scale of the 1 = 6 layer, and smaller errors in those for 1 = 5 and 1 = 7. These errors are attributable to the small numbers of data common to these layers and the precession layers. Hamilton, Rollett, and Sparks (1965) have shown that the method of Rollett and Sparks (1960) for correlating data is wrong, and leads to incorrect results when small numbers of data correlate the different layers. At this stage a Hilger linear diffractometer (Arndt and Phillips, 1961) became available, and it was decided to collect fresh data and use this to re-correlate the photographic data.

Refinement of diffractometer data and of rescaled photographic data.

3-dimensional data were collected on the linear diffractometer, using a crystal of similar dimensions to that used for the photographic data. MoKα radiation was used with

balanced Strontium and Zirconium filters. Intensities were measured with a scintillation counter, using pulse height discrimination. The data were corrected for Lorentz and polarisation factors using a Deuce computer programme written by J.G. Sime, giving a set of 391 structure amplitudes on a single scale.

The Weissenberg photographic data were then put on a single scale by comparison with the counter data.

Two parallel refinements were now carried out, starting from the parameters obtained in the previous stage of the refinement. The programme and weighting scheme were the same as those used previously. Four cycles were needed to produce convergence in each case, reducing the residuals to 0·074 for the photographic data and 0·060 for the counter data.

The two sets of final co-ordinates, which are not significantly different, together with the means of the two and their standard deviations are given in Table 2. The observed and calculated structure factors are given in Tables 3 and 4. The two sets of temperature factors, given in Table 5, show some significant differences, which may be attributable to absorption effects differing in the two crystals.

TABLE 2

FINAL CO-ORDINATES IN ANGSTROMS
(E.S.D.s IN BRACKETS ARE IN UNITS IN THE 3rd PLACE)

UPPER VALUES - DIFFRACTOMETER DATA,
LOWER VALUES - PHOTOGRAPHIC DATA.

ATOM	x	y	z
Zn	1.712(1)	1.727(1)	0
	1.711(1)	1.727(1)	0
Si	0	1.567(4)	2.606(7)
	0	1.578(4)	2.623(6)
O(1)	1.333(9)	2.213(9)	3.296(10)
	1.331(9)	2.220(9)	3.297(10)
O(2)	0	1.783(14)	1.020(12)
	0	1.802(12)	1.016(12)
O(3)	2.586(15)	0	0.128(45)
	2.573(16)	0	0.181(40)
O(4)	0	0	3.041(20)
	0	0	3.018(28)
O(5)	4.185(=.5)	0	2.599(61)
	4.185(=.5)	0	2.570(54)

MEANS

Zn	1.711(1)	1.727(1)	0
Si	0	1.572(3)	2.614(5)
O(1)	1.332(7)	2.216(7)	3.297(7)
O(2)	0	1.793(9)	1.018(9)
O(3)	2.580(11)	0	0.155(30)
O(4)	0	0	3.030(17)
O(5)	4.185(=.5)	0	2.584(40)

TABLE 3

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR PHOTOGRAPHIC DATA

H	K	L	Fo	Fc
0	4	0	89.8	99.3
0	6	0	188.4	219.6
0	8	0	18.7	19.2
0	10	0	68.9	71.0
0	12	0	71.6	70.6
0	14	0	20.4	20.2
0	16	0	44.9	38.6
0	18	0	29.8	25.9
1	3	0	144.7	147.9
1	5	0	38.6	42.5
1	7	0	45.9	46.9
1	9	0	37.4	40.6
1	13	0	28.2	26.8
2	2	0	79.6	71.8
2	4	0	46.8	47.0
2	6	0	83.5	89.7
2	8	0	34.7	31.4
2	10	0	31.3	28.7
2	12	0	44.2	43.8
2	16	0	19.6	21.3
2	18	0	19.4	21.2
3	1	0	37.6	32.9
3	3	0	135.0	130.0
3	5	0	51.2	46.6
3	9	0	57.3	55.4
3	15	0	32.0	28.6
4	0	0	122.8	118.3
4	4	0	71.1	71.4
4	6	0	92.0	90.2
4	10	0	48.5	50.6
4	12	0	35.4	37.2
5	1	0	98.8	97.1
5	3	0	189.4	194.3
5	5	0	46.8	46.7
5	7	0	84.7	88.7
5	9	0	93.4	96.8
5	13	0	53.2	47.2
5	15	0	34.9	33.3
6	0	0	101.2	94.5
6	2	0	26.9	28.5
6	4	0	15.8	14.6
6	6	0	50.2	49.6
6	8	0	25.5	25.4
7	3	0	63.6	64.3
7	7	0	35.7	36.3
7	9	0	54.1	57.1
7	13	0	23.5	20.5
7	15	0	36.6	29.6
8	0	0	41.7	39.0
8	2	0	21.1	18.3
8	4	0	10.7	13.2
8	6	0	35.7	36.7
8	8	0	20.4	19.6
8	12	0	24.8	24.3
9	1	0	38.1	36.5
9	3	0	56.1	51.9
9	7	0	57.3	51.0
9	9	0	37.8	36.2
9	13	0	34.7	30.0
10	0	0	84.7	83.4
10	2	0	22.6	22.8
10	4	0	50.2	50.3
10	6	0	76.2	72.6
10	10	0	46.8	41.2
10	12	0	49.3	42.5
11	3	0	14.8	18.2
12	0	0	28.9	25.3
12	4	0	13.8	19.4
12	6	0	25.7	26.3
12	10	0	38.3	33.4
14	4	0	19.4	19.1
14	6	0	15.3	23.6
15	3	0	31.0	30.7
0	3	1	130.6	141.4
0	5	1	48.5	51.2
0	7	1	81.8	90.8
0	9	1	85.4	96.0
0	11	1	29.4	30.6
0	13	1	43.7	43.8
0	15	1	50.0	48.2
0	17	1	14.6	12.1
0	19	1	19.9	21.7
1	0	1	12.1	10.4
1	2	1	12.1	11.6
1	4	1	27.2	28.6
1	6	1	14.3	16.4
1	8	1	25.2	26.2
1	10	1	10.2	13.4
1	12	1	18.4	19.0
1	18	1	18.0	19.7
1	16	1	11.4	5.8
2	1	1	178.9	145.7
2	3	1	145.6	147.8
2	5	1	54.6	52.5
2	7	1	108.2	119.0
2	9	1	76.7	80.6
2	13	1	57.5	59.0
2	15	1	25.7	25.6
2	17	1	11.9	5.9
2	19	1	22.1	22.7
3	0	1	142.8	137.6
3	2	1	74.8	70.8
3	4	1	118.0	116.2
3	6	1	104.1	109.4
3	8	1	14.3	16.3
3	10	1	74.8	73.6
3	12	1	47.6	49.0
3	16	1	29.6	29.3
4	1	1	13.1	13.8
4	3	1	68.4	60.8
4	5	1	30.8	28.6
4	7	1	10.7	10.2
4	9	1	23.5	24.6
4	15	1	16.0	15.8
5	0	1	108.5	103.2
5	2	1	69.4	65.6
5	4	1	74.3	70.7
5	6	1	81.1	80.4
5	8	1	38.8	38.2
5	10	1	48.3	49.2
5	12	1	48.8	47.4
5	14	1	17.4	16.8
5	16	1	29.1	29.4
5	18	1	20.1	22.9
6	1	1	11.2	10.1
6	3	1	7.3	10.0
6	11	1	14.1	17.5
6	17	1	17.7	13.5
7	0	1	121.6	125.5
7	2	1	59.0	55.6
7	4	1	73.6	70.3
7	6	1	86.4	86.0
7	8	1	11.4	8.7
7	10	1	51.9	52.4
7	12	1	34.9	35.0
7	14	1	11.6	13.4
7	16	1	29.1	30.0
8	1	1	54.1	50.4
8	3	1	66.0	64.9
8	5	1	21.8	23.5
8	7	1	49.0	49.5
8	9	1	35.7	36.9
8	11	1	10.9	4.5
8	13	1	30.8	31.3
9	0	1	32.3	34.4
9	2	1	23.0	21.9
9	4	1	11.4	12.1
9	6	1	22.8	24.0
9	8	1	14.6	15.5
10	1	1	29.8	28.0
10	3	1	48.0	52.3
10	5	1	29.6	28.4
10	7	1	21.4	20.4
10	9	1	33.5	33.5
11	0	1	14.6	13.7
12	1	1	34.0	32.6
12	3	1	55.1	52.5
12	5	1	18.2	17.1
12	7	1	35.2	32.5
12	9	1	29.8	30.3
13	0	1	30.8	32.1
13	4	1	11.9	16.4
13	6	1	21.1	22.6
0	4	2	47.8	52.0
0	4	2	99.8	106.1
0	6	2	148.3	157.3
0	10	2	70.4	78.8
0	12	2	59.2	64.2
0	14	2	16.2	16.3
0	16	2	35.4	33.2
0	18	2	17.2	19.8
1	1	2	39.3	36.3
1	3	2	74.3	72.4
1	5	2	19.9	21.8
1	7	2	41.7	45.4
1	9	2	30.1	31.6
1	11	2	10.7	10.7
1	13	2	21.8	22.4
2	0	2	146.4	122.7
2	2	2	68.2	59.8
2	4	2	63.4	60.0
2	6	2	95.4	97.7
2	8	2	31.8	30.5
2	10	2	34.2	36.9
2	12	2	51.7	53.1
2	16	2	18.0	21.4
2	18	2	21.1	24.4
3	1	2	48.5	45.2
3	3	2	105.4	101.6
3	5	2	33.0	32.2
3	7	2	46.1	43.6
3	9	2	64.3	68.7
3	11	2	21.1	20.2
3	13	2	19.9	21.3
3	15	2	38.1	35.7
4	0	2	101.7	93.2
4	2	2	30.3	28.0
4	4	2	45.1	46.3
4	6	2	61.6	58.7
4	8	2	8.0	10.0
4	10	2	37.0	37.1
4	12	2	19.4	20.2
5	1	2	73.0	72.2
5	3	2	158.5	143.3
5	5	2	25.7	26.9
5	7	2	70.2	77.4
5	9	2	74.3	77.0
5	13	2	46.1	44.8
5	15	2	31.0	29.2
6	0	2	55.8	50.9
6	2	2	9.9	13.9
6	4	2	19.6	19.5
6	6	2	29.8	29.9
6	8	2	10.7	8.5
6	10	2	15.0	16.9
7	1	2	39.6	38.3
7	3	2	77.4	78.0
7	5	2	33.5	32.5
7	7	2	29.4	28.5
7	9	2	50.5	50.6
7	11	2	10.4	11.3
7	13	2	20.8	22.8
7	15	2	27.9	28.4
8	0	2	46.6	45.4
8	2	2	22.8	21.9
8	4	2	13.8	15.5
8	6	2	41.7	39.6
8	8	2	19.4	18.9
8	12	2	31.6	28.8
9	1	2	31.6	29.8
9	3	2	51.2	48.0
9	5	2	11.6	10.7
9	7	2	37.8	35.1
9	9	2	23.5	23.6
9	13	2	25.2	22.3
10	0	2	78.4	74.8
10	2	2	27.4	27.5
10	4	2	38.3	39.0
10	6	2	58.5	56.7
10	10	2	34.9	32.2
10	12	2	31.6	29.0
12	0	2	40.0	39.0
12	2	2	13.6	18.7
12	4	2	15.8	18.5
12	6	2	35.4	33.2
12	12	2	12.6	22.0
13	3	2	11.6	18.3
14	0	2	17.2	24.8
15	3	2	17.7	28.0
0	1	3	51.2	63.7
0	3	3	114.3	120.5
0	5	3	61.9	63.4
0	7	3	36.9	36.3
0	9	3	53.6	55.3
0	11	3	19.6	18.8
0	13	3	31.0	30.5
0	15	3	30.6	27.9
0	19	3	26.7	22.6
1	0	3	31.6	35.5
1	2	3	12.4	11.6
1	4	3	12.6	13.4
1	6	3	15.5	15.6
1	8	3	17.0	16.7
2	1	3	109.2	101.7
2	3	3	151.2	148.2
2	5	3	47.6	47.9
2	7	3	84.2	82.3
2	9	3	70.6	73.2
2	13	3	46.4	45.8
2	15	3	22.3	24.2
3	0	3	22.8	20.8
3	2	3	160.9	153.2
3	4	3	89.6	83.9
3	6	3	86.6	79.4
3	8	3	97.3	97.6
3	10	3	23.5	22.2
3	12	3	48.5	51.1
3	16	3	34.0	34.2
3	18	3	30.8	29.0
4	1	3	10.9	11.0
4	3	3	17.0	19.0
4	9	3	18.9	21.0
4	11	3	10.7	11.2
5	0	3	91.8	86.2
5	2	3	47.3	41.0
5	4	3	42.7	40.1
5	6	3	66.2	66.4
5	8	3	27.2	27.9
5	10	3	27.4	28.8
5	12	3	37.6	36.5
5	14	3	7.3	9.4
5	16	3	18.7	20.7
5	18	3	19.6	17.4
6	1	3	9.2	8.9
6	3	3	9.4	9.2
6	5	3	19.6	19.1
6	7	3	21.1	21.2
6	11	3	6.5	11.7
7	0	3	100.5	92.7
7	2	3	38.1	36.5
7	4	3	68.0	69.4
7	6	3	77.4	77.7
7	8	3	8.5	7.2
7	10	3	56.3	53.4
7	12	3	43.7	40.2
7	16	3	25.0	23.4
8	1	3	45.4	42.2
8	3	3	66.8	66.8
8	5	3	20.1	21.5
8	7	3	42.7	40.8
8	9	3	39.3	40.3
8	13	3	19.9	22.4
9	0	3	11.9	10.8
9	6	3	16.7	15.7
10	1	3	18.0	18.7
10	3	3	31.3	31.5
10	5	3	9.4	11.9
10	7	3	28.7	24.9
10	9	3	35.4	32.5
11	0	3	16.5	14.6
11	6	3	7.3	7.6
12	1	3	28.6	26.8
12	3	3	46.8	44.2
12	5	3	7.5	8.6
12	7	3	38.6	34.7
12	9	3	35.7	32.6
12	13	3	23.0	24.7
13	0	3	26.0	25.2
13	4	3	20.1	19.9
13	6	3	23.3	24.0
13	8	3	22.8	23.8
14	1	3	40.3	44.4
14	3	3	83.2	90.8
14	5	3	98.8	108.2
14	8	4	13.8	15.4
0	2	4	70.2	70.1
0	12	4	51.9	53.9
0	14	4	9.9	6.4
0	16	4	30.3	29.5
0	18	4	16.2	17.1
1	1	4	21.1	23.2
1	3	4	53.6	57.0
1	5	4	7.8	7.4
1	7	4	35.9	39.1
1	9	4	33.5	32.7
1	13	4	16.5	18.6
2	0	4	67.0	61.4
2	2	4	26.2	27.6
2	4	4	34.4	34.8
2	6	4	61.2	57.4
2	8	4	18.3	16.0
2	10	4	24.2	26.9
2	12	4	41.5	38.7
2	16	4	15.3	17.0
2	18	4	16.2	19.1
3	1	4	29.4	29.0
3	3	4	46.4	40.5
3	5	4	17.2	16.3
3	7	4	34.0	32.5
3	9	4	45.6	44.6
3	11	4	15.3	16.0
3	13	4	21.6	19.3
3	15	4	31.6	27.1
4	0	4	83.5	76.1
4	2	4	34.4	30.2
4	4	4	42.5	37.6
4	6	4	47.1	46.4
4	10	4	29.6	28.8
4	12	4	9.4	14.5
4	16	4	19.2	16.8
4	18	4	20.1	4.7
5	1	4	56.3	54.2
5	3	4	111.9	106.1
5	5	4	21.1	20.6
5	7	4	65.0	61.6
5	9	4	69.6	68.9
5	13	4	41.7	38.6
5	15	4	30.8	27.7
5	19	4	16.5	16.6
6	0	4	23.5	22.6
6	2	4	9.7	8.1
6	4	4	26.2	24.2
6	6	4	23.5	21.6
6	8	4	12.1	8.6
6	10	4	22.6	20.8
7	1	4	29.8	27.8
7	3	4	53.2	49.7
7	5	4	29.1	25.5
7	7	4	21.1	19.4
7	9	4	34.7	30.2
7	13	4	18.4	19.1
7	15	4	19.4	18.9
8	0	4	27.9	26.2
8	2	4	11.6	12.7
8	6	4	28.2	24.3
8	8	4	13.3	10.6
8	12	4	21.4	21.2
9	1	4	24.8	28.8
9	3	4	51.0	46.6
9	5	4	13.1	11.6
9	7	4	23.5	22.6
9	9	4	20.4	22.2
10	0	4	67.2	63.9
10	2	4	29.6	28.3
10	4	4	34.7	32.0
10	6	4	50.7	45.8
10	10	4	30.6	26.4
10	12	4	19.6	21.8
10	16	4	16.5	19.2
12	0	4	33.2	30.9
12	2	4	15.0	15.0
12	6	4	21.8	25.4
14	0	4	27.9	23.0
14	4	4	16.2	16.9
14	6	4	16.5	19.8
15	1	4	16.5	14.3
15	3	4	28.4	27.4
0	1	5	28.4	39.6
0	3	5	65.5	77.4
0	5	5	40.3	36.3
0	7	5	32.5	37.0
0	9	5	50.0	51.1
0	11	5	13.1	18.2
0	13	5	30.8	25.3
0	15	5	31.8	27.8
1	0	5	17.2	20.8
1	4	5	7.8	8.4
1	6	5	18.7	17.3
2	1	5	42.0	50.1
2	5	5	82.0	80.6
2	7	5	19.9	17.6
2	9	5	45.4	49.7
2	11	5	43.7	45.9
2	13	5	29.4	30.4
2	15	5	11.4	17.4
3	0	5	81.1	74.8
3	2	5	45.9	38.1
3	4	5	52.4	49.6
3	6	5	55.3	54.6
3	10	5	33.0	36.4
3	12	5	22.6	23.8
3	16	5	20.4	19.7
4	1	5	14.8	12.6
4	3	5	23.3	23.6
4	5	5	14.3	14.4
4	9	5	12.6	17.1
5	0	5	73.8	66.0
5	2	5	31.8	27.6
5	4	5	31.6	27.7
5	6	5	53.6	54.1
5	8	5	21.8	20.2
5	10	5	23.8	23.2
5	12	5	35.2	34.6
6	5	5	14.3	14.3
6	7	5	9.0	11.2
7	0	5	63.4	58.8
7	2	5	25.0	25.9
7	4	5	45.6	42.2
7	6	5	48.5	46.1
7	10	5	37.8	35.4
7	12	5	25.0	23.0
7	16	5	21.1	19.2
8	1	5	23.5	23.6
8	3	5	43.7	41.1
8	7	5	26.4	24.8
8	9	5	28.2	25.0
9	0	5	23.3	22.7
9	6	5	20.6	18.8
10	1	5	17.7	17.9
10	3	5	32.8	32.6
10	5	5	15.0	16.2
10	9	5	15.5	17.7
10	9	5	30.3	26.9
12	1	5	16.0	17.7
12	3	5	34.4	31.3
12	7	5	20.6	23.1
12	9	5	20.8	21.6
0	2	6	30.1	38.9
0	4	6	42.5	50.3
0	6	6	59.2	66.6
0	8	6	9.4	12.1
0	10	6	38.1	40.9
0	12	6	26.4	29.8
0	16	6	33.2	24.5
1	1	6	16.2	17.8
1	3	6	38.1	41.6
1	5	6	7.5	6.7
1	7	6	17.4	21.4
1	9	6	17.4	19.4
2	0	6	43.7	42.7
2	2	6	23.8	23.3
2	4	6	23.3	19.4
2	6	6	38.8	36.1
2	8	6	9.7	14.0
2	10	6	10.9	14.5
2	12	6	26.7	23.2
3	1	6	23.8	22.2
3	3	6	39.6	35.1
3	5	6	27.2	23.8
3	9	6	20.8	21.6
4	0	6	41.7	39.8
4	2	6	18.7	12.6
4	4	6	33.2	29.1
4	6	6	33.2	30.2
4	10	6	22.8	28.6
5	1	6	41.2	35.9
5	3	6	75.0	69.8
5	5	6	18.9	16.4
5	7	6	45.9	40.0
5	9	6	47.6	42.6
5	13	6	29.1	25.2
6	0	6	28.9	26.7
6	2	6	13.1	11.7
6	4	6	17.0	15.6
6	6	6	20.8	17.5
7	1	6	19.9	16.9
7	3	6	29.1	27.2
7	5	6	10.9	10.4
7	7	6	19.9	21.0
7	9	6	27.2	26.8
8	0	6	21.8	18.6
8	2	6	15.5	9.6
8	4	6	11.2	8.0
8	6	6	20.4	18.7
9	1	6	16.2	15.1
9	3	6	33.2	27.8
9	7	6	21.8	21.9
9	9	6	18.4	18.6
10	0	6	45.6	39.1
10	2	6	12.4	15.3
10	4	6	33.2	27.0
10	6	6	40.8	33.7
10	10	6	23.8	23.8
10	12	6	24.0	20.8
0	1	7	10.7	14.6
0	3	7	23.5	31.6
0	5	7	6.9	8.3
0	7	7	20.1	23.7
0	9	7	28.2	30.5
0	13	7	16.2	17.1
0	15	7	17.0	19.4
1	2	7	26.2	31.9
1	4	7	44.9	50.6
2	3	7	33.0	35.7
2	5	7	33.2	35.0
2	9	7	16.2	23.2
2	15	7	12.1	16.4
3	0	7	42.0	41.9
3	2	7	17.0	17.6
3	4	7	36.2	35.6
3	6	7	29.8	30.0
3	10	7	31.0	30.0
3	12	7	22.6	24.4
5	0	7	34.9	30.2
5	2	7	11.4	11.3
5	4	7	14.8	14.8
5	6	7	29.4	26.9
5	12	7	20.1	20.9
7	0	7	53.9	47.2
7	2	7	21.4	22.1
7	4	7	26.2	25.1
7	6	7	37.4	34.7
7	10	7	20.1	22.2
8	1	7	14.3	17.1
8	3	7	27.4	30.0
10	3	7	16.2	20.3
12	3	7	24.2	27.9

TABLE 4

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR DIFFRACTOMETER DATA

H	K	L	Fo	Fc	H	K	L	Fo	Fc	H	K	L	Fo	Fc	H	K	L	Fo	Fc
0	4	0	88.9	99.6	6	3	1	12.0	10.1	3	2	3	88.0	87.2	10	0	4	72.0	70.2
0	6	0	199.3	220.2	6	5	1	10.8	11.1	3	4	3	86.2	83.2	0	3	5	68.7	77.1
0	8	0	11.5	15.4	6	7	1	10.8	11.6	3	6	3	98.4	97.1	0	11	5	19.0	20.4
0	10	0	74.6	72.2	6	9	1	11.0	13.2	3	8	3	23.0	22.5	0	13	5	26.7	27.8
0	12	0	75.1	70.1	6	11	1	19.0	18.2	3	10	3	55.2	53.3	1	2	5	6.8	8.6
1	1	0	45.4	79.7	7	0	1	133.7	129.5	3	12	3	35.6	33.0	1	4	5	5.2	7.6
1	3	0	142.1	148.7	7	2	1	61.0	58.0	4	1	3	10.0	9.9	1	6	5	16.2	18.6
1	5	0	39.3	37.6	7	4	1	78.8	73.9	4	3	3	10.6	10.2	1	8	5	14.2	13.7
1	7	0	47.4	47.0	7	6	1	93.2	89.3	4	5	3	7.6	3.8	2	1	5	45.2	49.2
1	9	0	40.8	39.2	7	8	1	7.6	8.5	4	7	3	18.2	17.9	2	3	5	84.6	85.3
1	11	0	9.8	9.1	7	10	1	60.4	55.0	4	9	3	21.7	23.0	2	5	5	19.8	17.2
1	13	0	29.1	26.5	8	1	1	58.1	53.2	4	11	3	12.0	13.2	2	7	5	50.5	51.5
2	0	0	130.0	125.0	8	3	1	70.6	67.0	4	13	3	6.8	9.8	2	9	5	49.3	48.2
2	2	0	78.6	74.8	8	5	1	27.6	24.6	5	0	3	93.5	88.2	3	0	5	80.5	77.0
2	4	0	48.8	48.6	8	7	1	56.8	52.2	5	2	3	46.2	43.4	3	2	5	44.4	40.0
2	6	0	89.3	91.4	9	0	1	37.6	38.9	5	4	3	42.4	41.0	3	4	5	53.5	52.7
2	8	0	36.6	35.5	9	2	1	22.8	23.0	5	6	3	72.0	69.8	3	6	5	56.6	55.0
2	10	0	30.5	30.5	9	4	1	10.4	12.3	5	8	3	32.0	30.7	3	10	5	39.4	39.8
2	12	0	49.7	48.2	9	6	1	26.6	27.1	5	10	3	31.6	30.6	3	12	5	26.5	24.1
3	1	0	35.0	33.8	10	1	1	30.7	29.6	5	12	3	45.8	40.5	4	1	5	12.2	13.2
3	3	0	133.7	130.4	11	0	1	12.9	14.3	6	1	3	11.9	10.7	4	3	5	24.0	21.6
3	5	0	51.8	50.3	0	4	2	99.2	105.1	6	3	3	12.4	11.3	4	5	5	14.7	17.0
3	9	0	59.4	59.8	0	6	2	150.1	160.3	6	5	3	21.8	22.4	4	7	5	11.2	10.4
3	11	0	12.6	12.8	0	10	2	82.9	79.0	6	7	3	21.4	21.8	4	9	5	19.0	18.0
3	13	0	15.0	13.9	0	12	2	71.0	66.0	6	9	3	6.5	5.1	5	0	5	64.0	69.2
4	0	0	127.3	120.3	1	1	2	34.1	36.3	6	11	3	11.2	14.6	5	2	5	31.8	29.7
4	2	0	7.6	10.2	1	3	2	74.2	72.6	7	0	3	101.3	96.5	5	4	5	30.3	28.6
4	4	0	72.9	71.7	1	5	2	21.0	22.9	7	2	3	33.1	38.4	5	6	5	62.4	57.6
4	6	0	94.6	90.1	1	7	2	44.2	44.8	7	4	3	76.8	73.7	5	8	5	22.8	21.3
4	8	0	11.4	10.6	1	9	2	31.8	32.8	7	6	3	84.1	80.2	5	10	5	26.2	24.1
4	10	0	55.0	51.1	1	11	2	10.7	11.4	7	8	3	6.7	6.5	6	5	5	18.6	15.6
4	12	0	40.1	34.6	1	13	2	26.1	22.6	7	10	3	62.4	56.4	6	7	5	10.6	12.5
5	1	0	104.2	98.0	2	2	2	63.4	59.7	8	1	3	48.3	44.9	7	0	5	65.3	62.1
5	3	0	198.2	198.1	2	4	2	61.0	59.8	8	3	3	72.2	69.5	7	2	5	26.9	27.9
5	5	0	48.6	45.0	2	6	2	99.2	98.6	8	5	3	23.4	22.4	7	4	5	47.4	46.1
5	7	0	95.1	90.5	2	8	2	31.6	31.2	8	7	3	47.7	43.1	7	6	5	53.0	48.9
5	9	0	103.0	97.2	2	10	2	39.7	37.1	8	9	3	42.4	40.9	8	1	5	25.8	24.4
6	0	0	102.1	97.2	2	12	2	60.7	54.5	9	0	3	12.4	10.9	8	3	5	46.0	43.8
6	2	0	28.7	26.7	3	1	2	47.1	44.0	9	2	3	6.9	2.7	8	7	5	28.5	26.2
6	4	0	15.4	14.0	3	3	2	107.7	103.1	9	4	3	10.6	11.3	9	0	5	22.6	23.3
6	6	0	53.0	49.9	3	5	2	35.0	32.8	9	6	3	18.8	17.6	9	2	5	7.2	10.0
6	8	0	6.5	2.0	3	7	2	46.2	42.9	10	1	3	20.1	20.4	9	4	5	9.1	9.2
6	10	0	6.1	7.2	3	9	2	72.2	69.8	10	3	3	34.5	34.8	0	4	6	47.7	55.0
7	1	0	27.0	28.5	3	11	2	19.3	19.9	10	5	3	9.5	13.7	0	6	6	68.6	69.6
7	3	0	69.8	66.5	3	13	2	24.3	22.0	11	0	3	17.6	16.6	0	8	6	11.4	12.2
7	5	0	12.4	12.3	4	0	2	100.4	94.5	0	4	4	88.2	95.1	0	10	6	46.2	43.4
7	7	0	36.2	38.5	4	2	2	31.2	28.6	0	6	4	108.6	110.8	0	12	6	17.5	30.0
7	9	0	65.1	60.7	4	4	2	48.4	47.1	0	8	4	13.0	13.2	1	7	6	20.4	21.2
8	0	0	42.2	40.6	4	6	2	63.4	61.0	0	10	4	75.2	72.7	1	9	6	22.0	20.2
8	2	0	21.4	21.0	4	8	2	8.4	9.9	0	12	4	59.2	54.4	2	2	6	19.4	22.5
8	4	0	12.5	14.5	4	10	2	39.9	38.3	1	1	4	18.2	24.8	2	4	6	19.6	17.2
8	6	0	36.0	39.2	4	12	2	20.6	21.1	1	3	4	53.6	59.4	2	6	6	40.2	39.5
8	8	0	22.2	22.2	5	1	2	76.2	72.6	1	5	4	6.9	7.6	2	10	6	10.8	14.4
9	1	0	39.6	38.0	5	3	2	152.4	147.6	1	7	4	38.0	39.9	2	12	6	31.8	27.0
9	3	0	60.6	54.9	5	5	2	25.2	26.7	1	9	4	34.1	33.6	3	3	6	39.1	38.7
10	0	0	96.4	88.8	5	7	2	81.6	78.8	1	11	4	9.6	9.2	3	7	6	13.5	10.4
0	1	1	75.3	84.0	5	9	2	83.6	80.2	1	13	4	20.2	18.9	4	0	6	41.3	40.9
0	3	1	127.4	141.9	5	11	2	5.1	6.4	2	0	4	67.6	65.2	4	2	6	16.0	16.1
0	5	1	48.6	52.8	6	0	2	53.8	50.1	2	2	4	25.8	25.0	4	4	6	32.3	33.3
0	7	1	86.3	89.1	6	2	2	11.0	13.2	2	4	4	35.0	32.6	4	6	6	31.9	31.6
0	9	1	97.6	97.0	6	4	2	21.7	19.5	2	6	4	62.7	60.8	5	1	6	39.2	38.6
0	11	1	33.3	31.1	6	6	2	31.6	30.0	2	8	4	15.9	17.1	5	3	6	79.2	75.4
0	13	1	48.3	44.8	6	8	2	9.4	9.6	2	10	4	29.6	26.5	5	5	6	18.8	16.5
1	0	1	12.1	9.6	6	10	2	19.4	17.5	2	12	4	46.4	42.4	5	9	6	49.7	45.8
1	2	1	11.1	11.9	7	1	2	41.7	40.6	3	1	4	28.9	27.2	6	0	6	30.1	27.6
1	4	1	28.8	28.6	7	3	2	83.7	80.6	3	3	4	45.6	41.1	6	2	6	15.8	14.3
1	6	1	15.8	16.9	7	5	2	35.8	34.6	3	5	4	19.6	18.2	6	4	6	17.2	16.0
1	8	1	25.6	26.4	7	7	2	29.8	30.8	3	7	4	34.2	32.8	6	6	6	18.1	16.5
1	10	1	10.6	12.7	7	9	2	58.6	53.3	3	9	4	49.3	46.7	7	1	6	19.2	17.6
1	12	1	19.6	18.7	7	11	2	15.7	12.2	3	11	4	16.4	18.0	7	3	6	31.0	28.2
1	14	1	22.2	19.4	8	0	2	48.6	47.7	4	0	4	79.9	78.3	7	5	6	15.2	11.8
2	1	1	151.4	147.0	8	2	2	21.5	23.2	4	2	4	34.7	33.2	7	7	6	27.3	22.8
2	3	1	146.0	147.5	8	4	2	13.9	16.5	4	4	4	42.6	41.0	8	0	6	24.1	22.0
2	5	1	55.2	53.4	8	6	2	45.1	41.8	4	6	4	49.4	46.4	8	2	6	13.3	10.6
2	7	1	119.6	121.4	8	8	2	20.5	19.7	4	10	4	31.8	31.1	9	1	6	19.3	16.9
2	9	1	82.4	80.6	9	1	2	31.8	31.6	4	12	4	14.2	12.8	9	3	6	33.6	31.8
2	13	1	65.2	60.0	9	5	2	12.0	10.4	5	1	4	58.1	55.8	0	3	7	14.6	28.6
3	0	1	142.7	137.4	0	3	3	110.2	119.3	5	3	4	116.4	111.7	0	7	7	19.7	25.7
3	2	1	75.2	73.0	0	5	3	65.0	68.6	5	5	4	19.5	18.5	0	9	7	36.5	33.6
3	4	1	121.2	119.2	0	7	3	38.2	37.7	5	7	4	67.2	64.0	0	11	7	14.8	12.0
3	6	1	108.6	108.7	0	9	3	59.8	58.3	5	9	4	70.4	66.1	2	7	7	33.3	39.7
3	8	1	15.9	15.6	0	11	3	24.5	22.9	5	11	4	8.3	7.3	2	9	7	25.7	37.7
3	10	1	78.8	76.8	0	13	3	35.9	32.9	6	0	4	23.0	23.4	3	2	7	14.8	16.7
3	12	1	51.8	48.9	1	0	3	30.2	34.7	6	2	4	10.2	10.5	3	4	7	36.4	40.0
4	1	1	12.7	13.3	1	2	3	12.8	13.8	6	4	4	27.3	25.9	3	6	7	38.7	41.9
4	3	1	67.1	64.2	1	4	3	11.8	14.4	6	6	4	22.4	21.9	3	10	7	33.2	34.5
4	5	1	30.0	27.5	1	6	3	17.3	16.6	6	8	4	12.8	9.2	4	3	7	8.9	8.0
4	7	1	8.8	8.8	1	8	3	18.3	19.0	7	1	4	32.7	29.6	5	2	7	13.5	12.4
4	9	1	28.7	26.9	1	10	3	7.4	7.3	7	3	4	55.9	52.9	5	4	7	20.9	14.8
4	11	1	10.4	10.7	1	12	3	9.0	9.6	7	5	4	31.0	28.8	5	6	7	33.8	28.8
5	0	1	108.6	106.4	2	1	3	104.8	103.2	7	7	4	21.2	19.8	5	8	7	14.6	9.5
5	2	1	69.2	65.7	2	3	3	149.5	151.1	7	9	4	35.3	33.0	5	10	7	14.4	16.8
5	4	1	74.2	70.7	2	5	3	49.7	48.3	8	0	4	29.8	28.1	5	0	7	56.6	54.5
5	6	1	86.0	83.8	2	7	3	84.8	85.1	8	2	4	13.1	12.6	7	2	7	26.9	25.6
5	8	1	42.2	39.4	2	9	3	75.1	72.8	8	4	4	11.2	8.4	7	4	7	28.3	29.6
5	10	1	51.8	50.2	2	11	3	3.4	2.0	9	1	4	27.6	27.1	7	6	7	42.6	38.4
5	12	1	55.0	49.6	2	13	3	52.9	47.0	9	3	4	55.3	51.2	8	7	7	23.5	21.2
6	1	1	14.8	11.3	3	0	3	158.6	156.2	9	5	4	11.2	12.4					

TABLE 5

TEMPERATURE FACTORS
UPPER VALUES - DIFFRACTOMETER DATA, LOWER VALUES - PHOTOGRAPHIC DATA
(E.S.D.s GIVEN IN BRACKETS ARE UNITS IN THE 4th PLACE)

ATOM	U11	U22	U33	2U23	2U31	2U12
Zn	0.0093(3) 0.0126(2)	0.0139(4) 0.0151(2)	0.0121(3) 0.0136(2)	-0.0025(12) -0.0027(11)	0.0012(10) -0.0039(9)	-0.0055(5) -0.0057(5)
Si	0.0106(10) 0.0124(7)	0.0115(10) 0.0134(8)	0.0064(8) 0.0077(9)	0.0056(30) -0.0010(24)	0 0	0 0
O(1)	0.0121(23) 0.0154(18)	0.0233(28) 0.0184(20)	0.0095(20) 0.0184(21)	0.0017(43) 0.0043(39)	-0.0042(39) -0.0053(38)	-0.0227(47) -0.0255(34)
O(2)	0.0118(37) 0.0125(23)	0.0383(52) 0.0187(30)	0.0032(29) 0.0105(30)	-0.0042(56) 0.0036(48)	0 0	0 0
O(3)	0.0284(49) 0.0287(42)	0.0117(39) 0.0121(25)	0.0805(118) 0.0979(133)	0 0	0.0053(126) 0.0143(141)	0 0
O(4)	0.0239(59) 0.0251(56)	0.0150(52) 0.0176(46)	0.0118(45) 0.0350(64)	0 0	0 0	0 0
O(5)	0.0489(116) 0.0891(169)	0.1419(265) 0.2423(333)	0.0465(121) 0.0056(54)	0 0	0 0	0 0

Discussion of the Structure

(a) General. Figure 1 shows a projection of the structure down the [001] axis. The space group is polar, and the arbitrary origin in the z-direction has been chosen by fixing the zinc atom at z=0. Zinc and O(1) are in general positions, Si, O(2) and O(3) are in special positions on mirror planes, and O(4) and O(5) are in special positions at the intersection of two mirror planes.

The structure is made up of silicon-oxygen and zinc-oxygen tetrahedra, linked together by shared corners. There are large cavities between the tetrahedra. The water molecules occupy the centres of the cavities, which are connected together in the z-direction to form channels extending through the crystal. It is possible to remove the water on heating, without destroying the crystal structure, and it is presumably the channel structure which permits this. The water molecule is probably hydrogen bonded to oxygen atoms of the framework. Figure 2 shows a projection down the $[00\bar{1}]$ axis of the tetrahedra in 4 unit cells. The vertices of the tetrahedra mark the oxygen positions, and the silicon and zinc atoms have been omitted. Silicon atoms lie at the centres of the small tetrahedra, and zinc atoms at the centres of the large ones. Alternate layers of

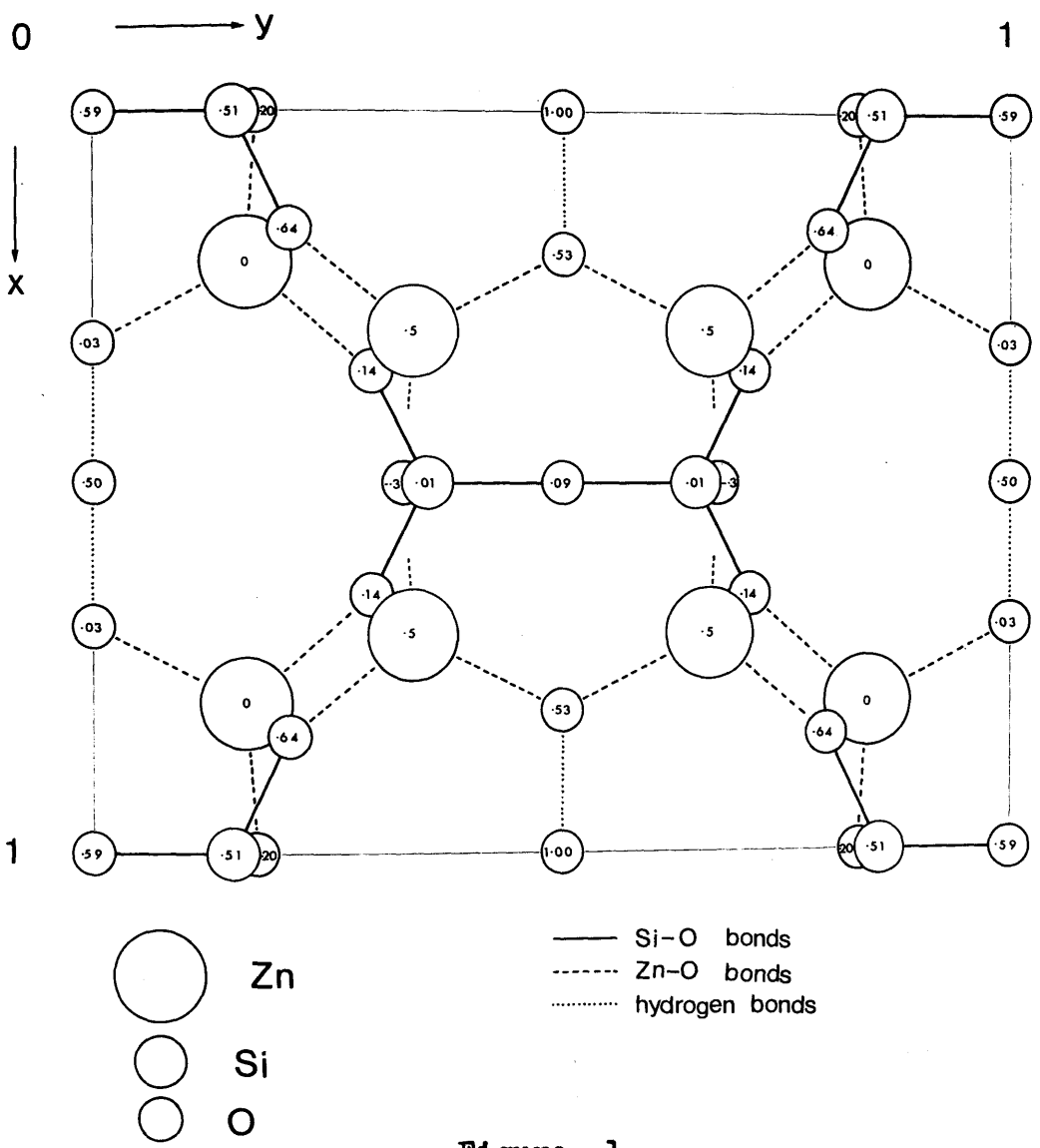

Figure 1.
Projection down the c-axis of the contents of one unit cell.

tetrahedra are related by the body-centering lattice translation.

An alternative way to consider the structure is to imagine it divided into layers by planes at y = 0, $\frac{1}{2}$, 1, etc. Each layer then consists of an infinite array of six membered rings. Each ring contains one silicon, two zinc, and three oxygen atoms, and all of the oxygens within the layer are three co-ordinate. The layers are then joined together by two co-ordinate oxygen bridges, Si-O(4)-Si and Zn-O(3)-Zn.

The bond lengths and angles, with their estimated standard deviations, are given in Table 6. These have been calculated from the averaged co-ordinates of Table 2.

(b) The Zinc Tetrahedron. The zinc-oxygen tetrahedron is fairly regular. The mean Zn-O distance of 1·955 Å may be compared with that found in the tetrahedral structure of zincite (ZnO). In the structure the mean length is 1·973 Å (calculated from the cell dimensions and not appreciably dependent on the single positional parameter of the structure). The slight shortening of 0·02 Å in hemimorphite may perhaps be associated with the fact that in hemimorphite the oxygens show trigonal co-ordination, whilst in zincite they are tetrahedrally co-ordinated.

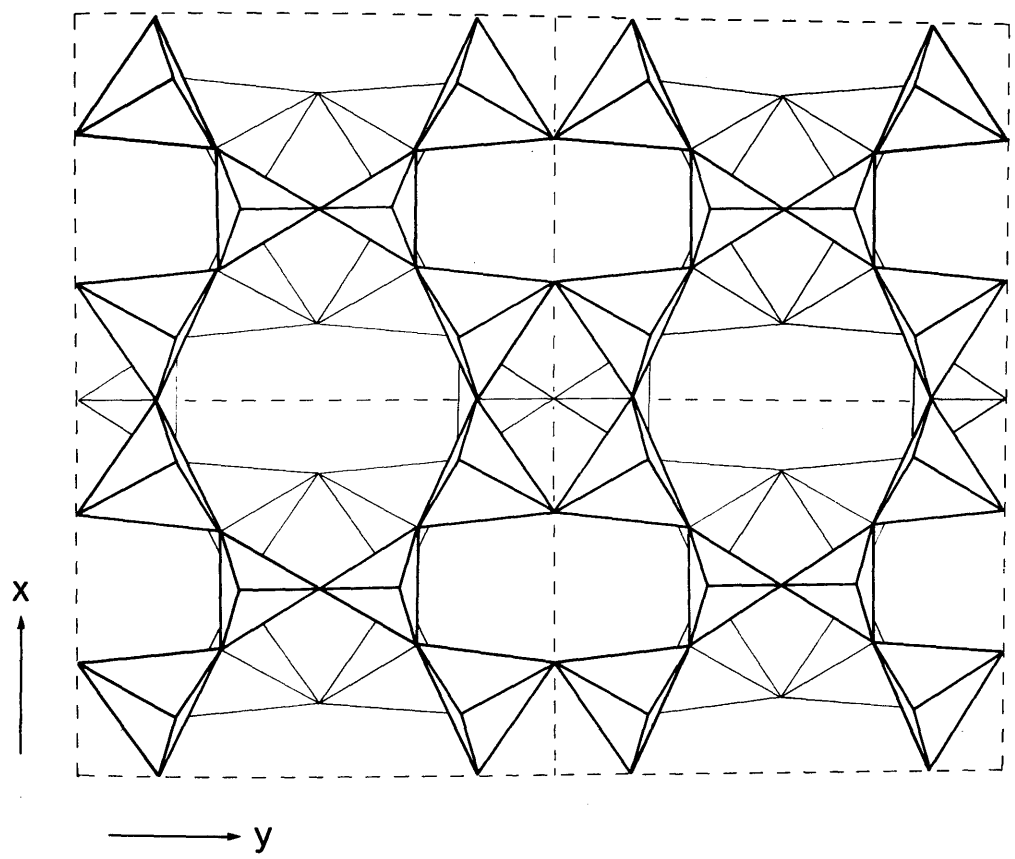

Figure 2.
c-axis projection of four unit cells,
showing the linking of the tetrahedra.

(c) The Si_2O_7 group. The Si_2O_7 group has crystallographic symmetry mm2. The unusual bond lengths and angles found by Barclay and Cox are not confirmed. The bridging Si-O distance of 1·626 Å, and the terminal Si-O distances of 1·630 and 1·611 Å are not significantly different. The bridging Si-O-Si angle of 150° is a fairly typical value.

A consideration of the π-bonding in an isolated $Si_2O_7^{6-}$ ion leads to the prediction that the terminal bonds should have a higher bond order, and should be shorter than the bridge bonds. However, there is clearly some covalent character in the Zn-O bonds, and arguments based on the assumption of an isolated $Si_2O_7^{6-}$ ion would clearly be invalid, since the lone pairs of electrons on the terminal oxygens, which would be used in π-bonding to the silicon, will be involved in bonding to the zinc. The covalent character of the Zn-O bonds is suggested by the observed bond angles at oxygen atoms O_1 and O_2, given in Table 6. Each of these atoms is linked to two zinc atoms and to one silicon, and the angles at oxygen are close to 120° suggesting sp^2 hybridisation at these oxygens. This leaves only one lone pair instead of two on the terminal oxygens available for π-bonding, and the bond lengths in the disilicate group

TABLE 6

BOND LENGTHS AND ANGLES
(ESTIMATED STANDARD DEVIATIONS IN BRACKETS)

BOND		ANGSTROMS
Zn - O(1)		1.925 (0.007)
Zn - O(1)*		1.963 (0.007)
Zn - O(2)		1.992 (0.005)
Zn - O(3)		1.940 (0.006)

ANGLE		DEGREES
O(1) - Zn - O(1)*		106.7 (0.3)
O(1) - Zn - O(2)		107.9 (0.3)
O(1) - Zn - O(3)		113.0 (0.9)
O(1)* - Zn - O(2)		106.5 (0.3)
O(1)* - Zn - O(3)		110.6 (0.5)
O(2) - Zn - O(3)		111.9 (0.6)

BOND		ANGSTROMS
Si - O(1)		1.630 (0.008)
Si - O(2)		1.611 (0.01)
Si - O(4)		1.626 (0.005)

ANGLE		DEGREES
Si - O(4) - Si		150.4 (1.2)
O(1) - Si - O(1)*		109.7 (0.4)
O(1) - Si - O(2)		111.2 (0.3)
O(1) - Si - O(4)		106.0 (0.7)
O(2) - Si - O(4)		112.7 (0.7)

ANGLE		DEGREES
Zn - O(1) - Si		117.2 (0.4)
Zn* - O(1) - Si		127.1 (0.4)
Zn - O(1) - Zn*		115.1 (0.4)
Zn - O(2) - Zn*		118.4 (0.5)
Zn - O(2) - Si		120.1 (0.2)
Zn - O(3) - Zn*		125.9 (0.6)

should therefore be more nearly equal.

(d) The Water Molecule and the Hydrogen Positions

The water molecule occupies a special position of mm2 symmetry at the centre of a cavity formed by 20 oxygen atoms of the tetrahedral framework. Figure 3 shows the y = 0 section through the centre of one of the cavities. The oxygen atoms lying on the y = 0 mirror plane are shown, and in addition the pairs of Zn atoms above and below the plane, which are bridged by O(3), are also marked. In order to understand the hydrogen bonding we need to postulate positions for two hydrogen atoms. One should be attached to the hydroxyl oxygen, O(3), and the other to the water oxygen, O(5). If the hydrogen bonds are to conform to the space group symmetry and also to acceptable stereochemistry for O(3) and O(5), the hydrogens must also lie on the y = 0 plane. The water molecules make contacts of 2·91 Å and 3·13 Å with hydroxyl oxygens, and no other contacts of less than 3·5 Å. The vibration of the water molecule is very high normal to the y = 0 plane, which is consistent with weak hydrogen bonds lying in the plane, with little restraint normal to the plane. If we assume that the O(3)-O(5) distance of 2·91 Å is a hydrogen bond, then the H-O-H angle is only 67° if the hydrogens lie on the line of the bond. The O-H-O bond is probably considerably bent,

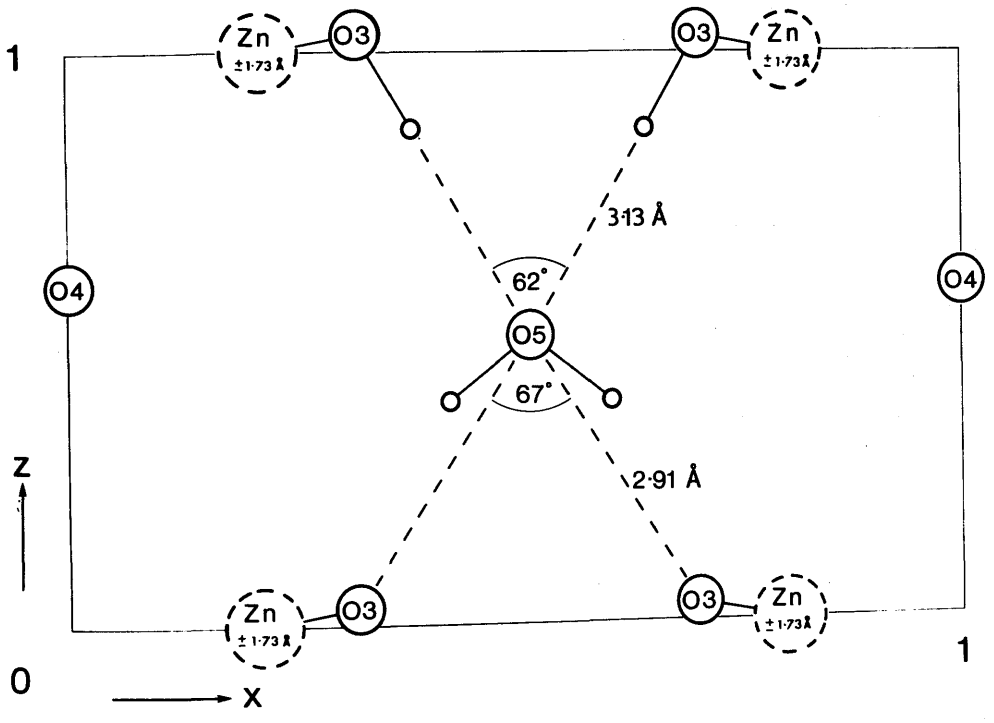

Figure 3.
Section of the cell at y = 0, showing the environment of the water molecule.

therefore. The hydrogen atoms of the hydroxyl groups are probably not involved in hydrogen bonds. Suggested positions for the hydrogen atoms are shown in Figure 3.

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CHAPTER 5

Refinement of the structure of sodium pyrophosphate decahydrate

The crystal structure of sodium pyrophosphate decahydrate was determined by MacArthur and Beevers (1957) from photographic data for three projections. These data were later used in a three-dimensional least-squares refinement by Cruickshank (1964). This refinement led to bond lengths in the pyrophosphate group with standard deviations of about 0·015 Å. In order to obtain more accurate dimensions fresh three-dimensional data were collected and a full refinement carried out.

Crystal Data

$Na_4P_2O_7 \cdot 10H_2O$, M = 446·06, Monoclinic, a = 17·01, b = 6·96, c = 14·85 Å, β = 112·0°. U = 1630 Å^3. Z = 4, D_c = 1·817, D_m (MacArthur and Beevers, 1957) = 1·817. F_{ooo} = 920.

Space Group C2/c.

Data Collection

Cell dimensions were measured from zero layer precession and Weissenberg photographs. The values obtained were a = 17·01 ±0.02, b = 6·96 ±0.01, c = 14·85 ±0.02 Å, β = 112·0 ±0·2°. These are in agreement with the values given by Corbridge (1957), and by MacArthur and Beevers (1957) for the I2/c cell.

Intensities were estimated visually from equi-inclination Weissenberg photographs of reciprocal lattice layers h0l to h5l, taken with Cu Kα radiation. They were corrected for Lorentz and polarisation factors using a Deuce computer programme written by J.G. Sime. This yielded a set of 1022 independent structure amplitudes, requiring 6 different scale factors. A structure factor calculation, using the co-ordinates and temperature factors of Cruickshank (1964) gave preliminary values for the layer scale factors and showed an initial residual ($R = \sum(|F_o| - |F_c|)/\sum|F_o|$) of 0·142.

Least Squares Refinement

The structure factor least-squares programme of J.G.F. Smith and D.W.J. Cruickshank for the KDF9 computer was used. The weighting scheme was $w = 1/(10 + F_o + 0{\cdot}005F_o^2)$. Two cycles of least squares refinement of co-ordinates, individual isotropic temperature factors and an overall scale factor reduced the residual to 0·098. This was followed by two cycles of block diagonal refinement in which anisotropic temperature factors were also refined. After correction of a small number of indexing errors and a further rescaling of the individual layers, two more cycles of least squares produced convergence, with a residual of 0·078.

An F_o-F_c Fourier synthesis was then computed. This showed peaks in the range $\pm$ 0·7 $e\text{Å}^{-3}$. Of about twenty peaks of height 0·5 to 0·7 $e\text{Å}^{-3}$, nine were in positions expected for hydrogen atoms. No peak could be found at the position expected for the remaining hydrogen, H(42). However, since the position of this atom was indicated by a short O - O distance of 2·8 Å, a probable position for the atom was calculated.

Two cycles of full matrix refinement of hydrogen atom co-ordinates and isotropic temperature factors were then carried out, followed by two cycles of block diagonal refinement in which the parameters of all atoms were allowed to vary. The residual was reduced to 0·072. No significant shifts of the heavy atoms occurred, although in every case the O - O hydrogen bond distance increased, by amounts varying from 0·001 to 0·007 Å. The hydrogen atom co-ordinates changed to produce, in general, more reasonable bond lengths and angles.

The final co-ordinates with their estimated standard deviations are given in Table 1. The atom numbering is the same as that used by MacArthur and Beevers. The temperature factors and their standard deviations are given in Table 2. The hydrogen atom parameters are listed separately in Table 3, and Table 4 gives the observed and calculated structure factors.

TABLE 1

FINAL FRACTIONAL CO-ORDINATES
(E.S.D.s IN BRACKETS ARE UNITS IN THE 4th PLACE)

ATOM	x	y	z
P	0.0657(1)	0.2710(3)	0.3477(1)
Na(1)	0.2413(2)	0.3065(5)	0.1069(2)
Na(2)	0.3848(2)	0.0845(5)	0.3016(2)
O(1)	0	0.1735(11)	1/4
O(2)	0.0254(3)	0.4484(8)	0.3702(3)
O(3)	0.0778(3)	0.1135(9)	0.4209(3)
O(4)	0.1447(3)	0.3223(8)	0.3272(3)
W(1)	0.1014(3)	0.3890(9)	0.0540(4)
W(2)	0.2405(3)	0.0212(8)	0.0214(4)
W(3)	0.2302(3)	0.0849(10)	0.2516(4)
W(4)	0.3926(3)	0.2647(8)	0.1710(4)
W(5)	0.4160(3)	0.3847(9)	0.3891(4)

TABLE 2

TEMPERATURE FACTORS
(E.S.D.s GIVEN IN BRACKETS ARE IN UNITS IN THE FOURTH PLACE)

ATOM	U11	U22	U33	2U23	2U31	2U12
P	0.0142(6)	0.0146(13)	0.0145(6)	0.0021(13)	0.0068(10)	0.0050(13)
Na(1)	0.0282(13)	0.0378(25)	0.0359(14)	0.0105(28)	0.0235(22)	0.0171(27)
Na(2)	0.0275(13)	0.0326(24)	0.0311(13)	0.0052(26)	0.0243(22)	0.0042(26)
O(1)	0.0299(32)	0.0145(51)	0.0236(30)	0	-0.0096(50)	0
O(2)	0.0260(21)	0.0119(34)	0.0320(22)	-0.0059(42)	0.0213(37)	0.0053(30)
O(3)	0.0374(25)	0.0357(41)	0.0223(22)	0.0189(44)	0.0196(39)	0.0021(49)
O(4)	0.0221(21)	0.0333(40)	0.0363(24)	-0.0178(46)	0.0319(38)	-0.0134(43)
W(1)	0.0237(21)	0.0535(46)	0.0268(23)	0.0065(49)	0.0193(37)	0.0116(49)
W(2)	0.0273(23)	0.0297(40)	0.0336(25)	0.0000(48)	0.0080(38)	-0.0053(47)
W(3)	0.0266(24)	0.0545(50)	0.0465(30)	-0.0309(56)	0.0352(47)	0.0051(53)
W(4)	0.0315(23)	0.0266(40)	0.0375(25)	0.0163(49)	0.0317(41)	0.0097(47)
W(5)	0.0413(28)	0.0402(45)	0.0331(25)	-0.0020(50)	0.0295(44)	-0.0024(54)

TABLE 3

HYDROGEN PARAMETERS

ATOM	x	y	z	U
H(11)	0.064(7)	0.417(16)	-0.012(8)	0.075(34)
H(12)	0.065(10)	0.408(24)	0.066(11)	0.136(66)
H(21)	0.192(5)	-0.065(13)	-0.005(6)	0.045(25)
H(22)	0.270(8)	0.003(20)	0.095(8)	0.092(40)
H(31)	0.193(10)	0.175(24)	0.257(11)	0.147(59)
H(32)	0.177(6)	0.006(16)	0.192(7)	0.074(31)
H(41)	0.432(6)	0.171(14)	0.152(6)	0.059(27)
H(42)	0.398(14)	0.327(32)	0.140(14)	0.215(88)
H(51)	0.467(8)	0.411(18)	0.410(8)	0.082(42)
H(52)	0.410(10)	0.413(26)	0.464(11)	0.180(68)

TABLE 4

OBSERVED AND CALCULATED STRUCTURE FACTORS

H	K	L	Fo	Fc	H	K	L	Fo	Fc	H	K	L	Fo	Fc	H	K	L	Fo	Fc
0	0	2	83.5	-81.2	14	0	2	44.2	-47.5	3	1	-6	140.4	-152.2	9	1	-18	16.4	14.3
0	0	4	131.1	-139.5	14	0	4	35.1	-34.8	3	1	-7	33.2	28.8	11	1	3	54.9	52.9
0	0	6	27.8	28.2	14	0	6	30.0	30.4	3	1	-8	73.6	-72.9	11	1	4	61.6	-59.5
0	0	8	23.6	19.4	14	0	-6	13.9	-12.5	3	1	-9	62.8	61.0	11	1	5	49.6	-46.3
0	0	10	25.7	-22.9	14	0	-8	40.7	39.5	3	1	-10	51.7	50.0	11	1	6	45.2	39.0
0	0	12	25.8	28.2	14	0	-10	43.6	-42.5	3	1	-16	28.4	-24.0	11	1	7	45.3	-38.6
2	0	0	61.6	58.6	14	0	-12	56.3	57.4	3	1	-17	25.6	-25.5	11	1	9	53.9	51.4
2	0	2	54.0	48.2	14	0	-14	49.4	46.5	5	1	0	54.9	53.2	11	1	11	17.5	16.7
2	0	4	190.1	-206.0	14	0	-16	51.3	-48.1	5	1	1	71.8	-73.4	11	1	-1	77.7	-75.6
2	0	6	39.9	-36.7	14	0	-18	23.1	-23.2	5	1	2	73.3	-75.6	11	1	-2	19.3	-17.1
2	0	8	68.6	63.4	16	0	0	39.8	39.8	5	1	3	37.5	34.6	11	1	-3	40.0	38.8
2	0	10	105.8	-108.7	16	0	2	29.7	30.1	5	1	4	105.0	107.9	11	1	-4	28.6	-22.1
2	0	12	38.7	-37.1	16	0	4	14.4	-16.1	5	1	7	65.2	70.6	11	1	-5	33.3	33.2
2	0	14	100.0	96.4	16	0	6	28.3	28.9	5	1	8	55.2	-56.7	11	1	-6	69.2	-67.7
2	0	-2	135.6	-122.6	16	0	-2	66.9	-71.6	5	1	9	31.4	-31.0	11	1	-7	45.3	-39.7
2	0	-4	36.3	-30.8	16	0	-4	16.4	-16.5	5	1	10	36.8	-38.9	11	1	-8	26.2	-26.6
2	0	-6	131.8	130.2	16	0	-6	16.5	17.5	5	1	11	62.2	-62.0	11	1	-9	80.4	86.4
2	0	-8	132.3	-136.2	16	0	-12	7.6	9.0	5	1	13	29.3	25.5	11	1	-10	40.9	39.8
2	0	-12	54.5	53.9	16	0	-14	25.2	23.2	5	1	15	27.4	27.5	11	1	-12	17.9	-18.8
2	0	-14	23.0	-21.8	16	0	-16	49.1	-49.2	5	1	-1	91.7	88.5	11	1	-13	92.5	-94.9
2	0	-16	14.0	-13.3	18	0	2	12.6	-9.6	5	1	-2	22.1	-21.8	11	1	-15	29.8	26.0
4	0	0	28.0	-25.6	18	0	-2	48.1	-47.0	5	1	-3	88.4	-88.0	11	1	-17	29.4	28.0
4	0	2	142.9	144.9	18	0	-4	30.2	27.8	5	1	-4	126.3	123.9	11	1	-18	13.7	13.5
4	0	6	138.3	-139.0	18	0	-6	33.2	31.1	5	1	-5	32.3	-30.3	13	1	0	67.1	66.1
4	0	8	174.4	192.5	18	0	-8	56.8	-54.7	5	1	-6	33.4	32.3	13	1	1	107.1	-122.4
4	0	10	19.9	-19.5	18	0	-10	20.4	-17.3	5	1	-7	11.0	9.3	13	1	3	48.2	45.7
4	0	12	41.2	-39.1	18	0	-12	64.4	64.4	5	1	-8	13.4	-13.5	13	1	4	17.7	18.2
4	0	14	21.4	22.5	20	0	0	5.7	-6.4	5	1	-9	65.9	-61.1	13	1	5	21.8	21.5
4	0	16	23.0	23.8	20	0	-2	23.5	-20.5	5	1	-10	35.4	32.0	13	1	7	33.5	-31.5
4	0	-2	53.1	-52.3	20	0	-4	11.7	9.5	5	1	-13	81.7	88.0	13	1	9	15.3	15.7
4	0	-4	100.4	94.9	20	0	-6	40.9	39.7	5	1	-14	16.0	-13.1	13	1	-1	34.6	32.8
4	0	-6	57.6	-51.6	20	0	-8	47.5	-47.8	5	1	-15	27.9	-25.7	13	1	-2	21.6	-17.9
4	0	-8	136.1	135.3	20	0	-10	5.6	-4.8	5	1	-16	25.7	22.5	13	1	-3	54.7	52.1
4	0	-12	56.1	53.9	20	0	-12	9.6	11.8	5	1	-17	21.6	-19.5	13	1	-4	26.2	27.0
4	0	-14	67.3	-69.2	1	1	0	65.2	-63.2	7	1	0	98.7	-98.1	13	1	-5	38.6	-36.0
4	0	-16	34.3	-33.0	1	1	1	92.1	-101.4	7	1	1	111.0	114.5	13	1	-6	43.1	-41.2
4	0	-18	12.3	12.4	1	1	2	53.1	46.7	7	1	2	64.7	-65.2	13	1	-7	15.4	-12.1
6	0	0	234.9	-289.7	1	1	3	101.3	-96.3	7	1	4	33.8	30.5	13	1	-9	41.1	39.1
6	0	4	42.5	45.4	1	1	4	7.3	9.2	7	1	5	54.5	-55.2	13	1	-10	40.8	39.3
6	0	6	21.2	17.9	1	1	5	56.9	59.2	7	1	7	40.0	38.2	13	1	-11	36.0	-32.6
6	0	12	43.7	-41.5	1	1	6	50.2	-45.9	7	1	8	21.0	19.7	13	1	-15	36.5	34.7
6	0	14	19.9	-17.7	1	1	7	10.2	7.1	7	1	11	37.3	-32.7	13	1	-16	31.1	28.0
6	0	-2	136.3	-138.5	1	1	8	27.3	-25.7	7	1	14	21.3	22.5	15	1	2	15.4	-16.3
6	0	-4	95.0	95.3	1	1	9	83.4	-89.0	7	1	-1	41.1	36.2	15	1	5	25.7	25.0
6	0	-6	23.9	21.1	1	1	10	12.9	-12.9	7	1	-2	96.6	104.2	15	1	7	19.2	-18.8
6	0	-10	34.7	-31.2	1	1	11	64.2	64.9	7	1	-3	86.7	-88.0	15	1	-1	62.8	63.1
6	0	-12	35.5	28.9	1	1	12	27.8	25.3	7	1	-4	34.8	-34.5	15	1	-2	48.2	44.9
6	0	-14	29.7	28.1	1	1	13	34.6	30.7	7	1	-5	27.4	-23.9	15	1	-3	30.0	-27.6
6	0	-18	13.3	16.4	1	1	14	34.5	-29.1	7	1	-6	31.9	30.0	15	1	-4	52.6	-55.3
8	0	0	109.1	102.2	1	1	15	22.5	-19.8	7	1	-7	37.7	37.1	15	1	-5	81.8	-89.0
8	0	2	46.2	43.4	1	1	17	10.7	-8.4	7	1	-8	39.6	-37.6	15	1	-6	19.7	-21.1
8	0	4	74.7	73.1	1	1	-1	78.4	65.5	7	1	-9	41.1	-40.4	15	1	-7	53.9	55.1
8	0	6	29.1	-28.3	1	1	-2	20.8	20.7	7	1	-10	36.8	-34.5	15	1	-8	25.4	-26.8
8	0	10	73.4	72.0	1	1	-3	7.3	-5.8	7	1	-11	36.7	35.4	15	1	-9	21.2	17.6
8	0	-2	129.6	-135.0	1	1	-4	25.6	21.1	7	1	-12	13.5	-15.0	15	1	-10	11.3	14.6
8	0	-4	66.6	63.1	1	1	-5	57.7	54.7	7	1	-13	22.7	21.8	15	1	-11	36.9	-32.6
8	0	-6	16.7	-19.3	1	1	-6	97.0	-98.2	7	1	-14	28.9	-30.0	15	1	-14	20.7	-17.2
8	0	-10	25.4	22.6	1	1	-7	16.5	14.7	7	1	-15	73.1	-71.8	15	1	-15	19.0	16.9
8	0	-12	62.1	-65.4	1	1	-8	80.1	82.5	7	1	-17	24.7	21.0	17	1	3	35.9	-34.1
8	0	-14	23.2	-23.8	1	1	-9	26.5	23.2	9	1	0	19.5	-17.4	17	1	4	16.8	13.3
8	0	-16	64.1	58.4	1	1	-10	35.0	33.5	9	1	1	6.4	5.7	17	1	5	14.8	15.7
10	0	0	24.3	-22.9	1	1	-11	73.9	-80.0	9	1	2	25.0	-23.4	17	1	-1	45.7	40.7
10	0	2	63.2	-64.6	1	1	-12	42.0	43.0	9	1	3	18.5	14.4	17	1	-2	15.1	17.3
10	0	4	55.4	51.4	1	1	-13	19.7	19.0	9	1	5	31.6	-31.7	17	1	-6	11.0	12.3
10	0	6	44.3	-46.2	1	1	-15	43.8	43.5	9	1	6	13.7	-15.4	17	1	-7	13.4	-14.6
10	0	8	49.3	-44.8	1	1	-16	9.1	-7.2	9	1	7	39.4	38.1	17	1	-8	47.5	41.0
10	0	10	13.7	18.4	1	1	-17	23.4	-23.5	9	1	8	13.8	14.5	17	1	-10	27.8	-23.3
10	0	-2	36.4	39.8	3	1	1	92.4	92.4	9	1	9	10.9	-12.3	17	1	-11	27.0	-21.5
10	0	-4	41.9	40.0	3	1	2	24.7	-22.5	9	1	10	25.9	-19.3	17	1	-13	38.8	34.2
10	0	-8	54.9	-56.2	3	1	3	94.8	-103.0	9	1	11	24.7	-21.0	17	1	-14	19.6	-15.9
10	0	-10	17.2	-17.9	3	1	4	54.4	50.4	9	1	12	24.9	20.9	17	1	-15	7.4	9.8
10	0	-12	40.8	-40.6	3	1	5	52.1	-49.2	9	1	13	18.3	-17.4	19	1	0	15.0	-13.5
10	0	-14	32.6	29.2	3	1	6	107.2	115.7	9	1	-1	98.2	-104.7	19	1	1	33.1	32.4
10	0	-16	71.2	69.7	3	1	7	40.6	37.1	9	1	-2	19.5	18.8	19	1	-3	37.7	-33.3
10	0	-18	37.8	-34.3	3	1	8	42.3	-40.8	9	1	-3	20.2	19.6	19	1	-7	26.7	24.5
12	0	0	62.7	62.0	3	1	9	10.5	10.9	9	1	-4	58.5	60.3	19	1	-8	23.8	19.3
12	0	2	8.0	-5.6	3	1	11	16.0	13.9	9	1	-5	172.7	195.0	19	1	-11	27.2	-22.8
12	0	4	14.3	16.9	3	1	12	8.0	8.6	9	1	-6	25.5	24.3	19	1	-12	24.1	-20.8
12	0	6	43.1	-40.7	3	1	13	25.3	25.6	9	1	-7	102.3	-105.7	21	1	-3	17.3	-20.3
12	0	10	14.2	15.8	3	1	15	20.5	-17.4	9	1	-8	94.1	105.4	21	1	-5	30.6	31.1
12	0	-2	88.5	91.0	3	1	16	19.9	19.4	9	1	-9	33.8	-31.0	21	1	-7	12.3	11.6
12	0	-4	83.3	-82.4	3	1	-1	139.6	174.0	9	1	-10	46.6	-48.9	21	1	-8	15.9	16.9
12	0	-8	86.2	88.5	3	1	-2	28.0	-27.2	9	1	-11	34.3	31.4	21	1	-9	29.9	-29.9
12	0	-10	53.9	-52.8	3	1	-3	134.1	-151.4	9	1	-12	25.1	23.8	0	2	1	13.7	14.0
12	0	-12	29.7	-28.5	3	1	-4	17.5	-13.7	9	1	-15	30.7	-28.5	0	2	2	89.8	87.2
12	0	-18	21.7	-21.7	3	1	-5	106.5	-107.2	9	1	-17	31.5	29.8	0	2	3	149.1	175.5

TABLE 4

(CONTINUED)

H	K	L	Fo	Fc	H	K	L	Fo	Fc	H	K	L	Fo	Fc	H	K	L	Fo	Fc
0	2	4	131.0	133.8	6	2	-9	35.2	36.2	14	2	-2	27.7	-28.7	3	3	-2	51.0	-48.4
0	2	5	111.6	-115.3	6	2	-10	14.4	-14.6	14	2	-3	11.3	14.0	3	3	-3	14.8	-13.3
0	2	6	64.0	-59.8	6	2	-11	56.9	64.7	14	2	-4	29.7	30.6	3	3	-4	9.5	9.8
0	2	8	12.9	7.6	6	2	-12	27.3	-27.9	14	2	-5	25.1	27.8	3	3	-5	13.1	13.8
0	2	9	35.0	30.5	6	2	-13	19.7	-20.4	14	2	-6	19.5	-18.7	3	3	-6	50.5	44.7
0	2	10	51.9	51.3	6	2	-14	45.6	43.6	14	2	-7	57.1	-62.2	3	3	-7	69.1	-64.7
0	2	12	51.4	-52.0	6	2	-15	15.1	-16.2	14	2	-9	16.1	16.6	3	3	-8	20.0	-18.8
0	2	15	21.4	-15.7	6	2	-16	9.7	-10.6	14	2	-10	32.0	35.3	3	3	-9	15.2	13.1
0	2	16	33.8	34.3	6	2	-17	33.7	-30.4	14	2	-14	29.6	-28.7	3	3	-10	25.7	-25.1
0	2	17	30.4	-31.6	6	2	-18	6.5	-8.2	16	2	0	39.7	-39.7	3	3	-11	72.6	84.4
2	2	0	48.2	-46.6	8	2	0	47.6	49.8	16	2	4	33.2	33.9	3	3	-12	37.8	-34.1
2	2	1	97.2	85.4	8	2	1	94.1	-96.4	16	2	-2	22.1	20.8	3	3	-13	50.2	-54.5
2	2	2	113.9	-102.7	8	2	2	25.0	19.9	16	2	-4	44.8	46.1	3	3	-17	21.0	22.6
2	2	3	90.6	93.2	8	2	3	64.1	72.9	16	2	-5	19.4	20.4	5	3	0	10.2	-10.1
2	2	4	21.1	23.7	8	2	4	17.5	-14.9	16	2	-6	38.0	-35.0	5	3	1	57.8	-54.6
2	2	5	114.3	-116.4	8	2	5	43.1	44.4	16	2	-8	33.3	-34.4	5	3	2	29.2	-26.9
2	2	6	72.9	-77.4	8	2	6	56.2	58.3	16	2	-10	36.5	36.8	5	3	3	70.1	67.9
2	2	7	15.6	-12.9	8	2	8	30.0	24.7	16	2	-11	23.4	23.9	5	3	4	39.6	-36.6
2	2	8	55.7	-60.5	8	2	9	15.7	-13.5	16	2	-12	17.3	-18.0	5	3	5	30.9	-28.6
2	2	9	50.7	51.9	8	2	10	31.4	-29.5	16	2	-13	9.4	-14.0	5	3	7	26.0	-23.9
2	2	10	77.9	85.1	8	2	-1	46.2	-44.0	18	2	0	17.0	-14.3	5	3	9	21.3	18.4
2	2	11	19.6	-18.8	8	2	-2	38.2	-39.5	18	2	1	25.8	-29.2	5	3	10	24.3	22.7
2	2	12	16.0	-15.6	8	2	-3	72.9	-71.4	18	2	2	15.3	-13.9	5	3	12	28.1	-29.2
2	2	14	31.3	-32.3	8	2	-4	36.5	33.6	18	2	3	9.3	9.1	5	3	13	18.4	-14.9
2	2	16	16.0	15.3	8	2	-5	83.9	77.6	18	2	-1	20.2	21.0	5	3	-1	77.6	64.5
2	2	-1	42.7	39.2	8	2	-6	66.7	63.1	18	2	-2	9.4	12.1	5	3	-2	79.2	92.8
2	2	-2	148.1	156.9	8	2	-7	15.6	15.5	18	2	-5	22.4	-22.5	5	3	-3	17.5	-15.1
2	2	-3	133.0	135.1	8	2	-8	31.4	-29.4	18	2	-6	20.1	-21.0	5	3	-4	15.1	12.8
2	2	-4	184.0	-214.5	8	2	-9	24.5	22.0	18	2	-7	10.0	-14.2	5	3	-5	132.9	-132.4
2	2	-5	132.2	-129.3	8	2	-10	60.2	-62.3	18	2	-8	22.1	23.1	5	3	-6	8.7	-9.6
2	2	-6	42.9	-40.4	8	2	-14	50.0	52.5	18	2	-9	9.6	9.7	5	3	-7	61.3	-55.0
2	2	-7	45.5	-36.4	8	2	-15	10.6	10.1	18	2	-10	26.4	24.9	5	3	-8	20.2	-16.8
2	2	-8	65.0	65.8	8	2	-16	37.7	-36.0	18	2	-11	36.8	38.3	5	3	-9	73.3	73.6
2	2	-9	43.2	-39.1	8	2	-17	8.5	-9.7	18	2	-12	30.7	-31.3	5	3	-10	47.2	48.8
2	2	-10	28.1	26.4	8	2	-18	17.6	-17.4	20	2	-1	21.5	-19.3	5	3	-11	44.0	46.3
2	2	-12	48.4	-51.0	10	2	0	41.8	37.1	20	2	-2	40.3	43.9	5	3	-12	38.7	38.9
2	2	-13	19.6	20.1	10	2	1	67.0	-72.6	20	2	-3	12.5	13.3	5	3	-13	40.5	-41.4
2	2	-16	25.5	24.0	10	2	2	38.2	36.4	20	2	-4	21.2	-21.4	5	3	-17	33.1	32.2
2	2	-17	14.5	11.1	10	2	3	35.6	34.6	20	2	-8	13.0	11.3	7	3	0	22.6	-19.0
4	2	0	66.1	56.8	10	2	4	56.4	-60.4	20	2	-10	16.8	-16.0	7	3	1	38.2	-36.3
4	2	1	54.0	49.3	10	2	5	19.5	19.3	20	2	-12	14.2	-16.4	7	3	2	40.2	39.3
4	2	2	66.3	-63.3	10	2	6	41.7	-41.8	1	3	0	19.2	-15.5	7	3	3	37.8	35.9
4	2	3	71.6	61.7	10	2	7	27.4	24.5	1	3	1	59.7	67.3	7	3	4	21.7	17.2
4	2	4	59.8	56.2	10	2	8	21.4	19.5	1	3	2	35.8	-33.2	7	3	5	56.0	54.0
4	2	5	86.8	-85.0	10	2	-2	65.9	-70.7	1	3	3	90.9	-97.6	7	3	8	21.3	-22.8
4	2	6	80.8	92.1	10	2	-3	9.2	9.2	1	3	4	68.6	-70.3	7	3	9	39.8	-35.5
4	2	7	47.2	-46.7	10	2	-4	59.3	-58.0	1	3	5	77.3	-70.5	7	3	10	19.7	20.8
4	2	8	34.8	-33.9	10	2	-5	45.0	-48.1	1	3	6	52.2	52.8	7	3	12	15.3	12.1
4	2	9	44.8	-45.9	10	2	-6	78.1	82.6	1	3	7	26.4	-22.2	7	3	-2	41.9	-41.4
4	2	10	22.7	-20.1	10	2	-7	26.1	25.6	1	3	8	10.8	-9.9	7	3	-3	144.6	140.9
4	2	11	57.0	52.7	10	2	-8	30.6	-26.7	1	3	9	45.3	48.1	7	3	-4	43.4	-40.1
4	2	12	44.1	45.0	10	2	-9	37.3	-40.0	1	3	10	34.0	-38.3	7	3	-5	136.6	-134.7
4	2	13	19.9	-18.2	10	2	-10	18.9	-17.1	1	3	11	27.4	30.9	7	3	-6	21.1	-16.3
4	2	14	19.3	-20.0	10	2	-12	35.9	36.2	1	3	12	17.1	-19.5	7	3	-7	19.9	18.1
4	2	-1	96.7	80.5	10	2	-13	33.9	33.5	1	3	13	28.2	-26.0	7	3	-8	47.7	-46.0
4	2	-2	78.5	80.2	10	2	-16	16.4	-16.9	1	3	15	25.2	25.9	7	3	-9	39.2	41.3
4	2	-4	45.1	-38.3	10	2	-18	25.8	25.2	1	3	16	16.1	-16.4	7	3	-10	28.5	26.8
4	2	-5	16.3	12.1	12	2	0	28.8	-29.2	1	3	-1	23.0	-18.2	7	3	-11	47.4	-49.3
4	2	-6	73.9	64.9	12	2	1	24.8	25.8	1	3	-2	42.3	40.7	7	3	-12	12.3	-14.1
4	2	-7	36.2	-31.0	12	2	2	53.4	52.7	1	3	-3	16.0	-15.8	7	3	-14	16.7	-18.3
4	2	-8	49.6	52.9	12	2	3	19.7	20.6	1	3	-4	54.4	70.4	7	3	-15	31.1	31.3
4	2	-9	54.1	54.4	12	2	6	15.1	-17.6	1	3	-5	57.1	50.3	7	3	-16	13.8	16.3
4	2	-10	64.7	-65.3	12	2	8	37.2	40.1	1	3	-6	57.7	58.6	7	3	-17	16.2	-15.0
4	2	-11	39.4	-42.3	12	2	9	28.9	-28.5	1	3	-7	56.8	-57.8	9	3	0	10.4	-9.1
4	2	-12	11.2	-10.5	12	2	-1	18.5	-18.6	1	3	-8	52.3	-48.6	9	3	1	21.5	-19.3
4	2	-13	19.7	21.1	12	2	-4	55.2	52.4	1	3	-9	29.2	29.7	9	3	3	49.6	-50.9
4	2	-14	31.6	29.7	12	2	-5	37.0	36.6	1	3	-11	24.3	28.4	9	3	5	27.2	27.9
4	2	-15	21.1	-18.5	12	2	-6	45.4	43.7	1	3	-12	30.1	29.3	9	3	6	21.3	17.4
4	2	-18	30.1	-30.2	12	2	-7	18.6	19.7	1	3	-13	26.8	-25.0	9	3	9	53.8	-53.1
6	2	0	39.6	40.0	12	2	-8	72.8	-79.0	1	3	-15	20.0	-20.3	9	3	11	23.0	24.0
6	2	2	24.6	20.1	12	2	-9	27.2	-31.2	1	3	-16	14.2	-14.7	9	3	-1	50.2	50.8
6	2	3	89.9	-91.5	12	2	-10	15.9	-14.6	1	3	-17	17.9	21.5	9	3	-2	79.1	83.9
6	2	4	119.2	-129.1	12	2	-11	48.9	-54.8	3	3	0	79.4	-75.4	9	3	-3	31.3	-28.2
6	2	5	51.4	50.9	12	2	-12	46.6	49.5	3	3	2	83.3	82.9	9	3	-4	33.1	29.3
6	2	6	46.0	42.4	12	2	-13	27.1	24.3	3	3	3	23.8	-19.5	9	3	-5	28.7	-27.1
6	2	8	19.3	-19.1	12	2	-14	28.1	-26.5	3	3	4	8.3	-5.1	9	3	-6	74.8	-76.9
6	2	10	29.7	-23.9	12	2	-16	21.7	-21.3	3	3	5	43.0	39.3	9	3	-7	51.7	49.4
6	2	11	24.0	20.0	12	2	-17	21.3	20.3	3	3	6	39.3	-39.9	9	3	-9	66.5	67.0
6	2	12	27.8	28.4	12	2	-18	16.2	16.7	3	3	7	42.4	-40.1	9	3	-10	77.9	79.0
6	2	-2	84.6	-77.4	14	2	0	46.2	-48.2	3	3	9	56.3	57.4	9	3	-11	91.7	-107.3
6	2	-3	9.5	5.0	14	2	1	27.7	29.5	3	3	10	24.5	27.5	9	3	-13	17.1	15.9
6	2	-4	102.7	-106.5	14	2	2	50.6	49.2	3	3	12	11.6	15.8	9	3	-15	21.5	22.1
6	2	-5	41.1	39.9	14	2	3	32.6	-34.1	3	3	13	26.1	-25.1	9	3	-17	25.1	-27.7
6	2	-6	24.7	22.7	14	2	5	30.8	-30.9	3	3	14	27.6	27.4	11	3	0	48.1	-49.8
6	2	-7	76.6	-76.6	14	2	6	46.8	-49.5	3	3	15	20.1	20.5	11	3	1	23.8	23.2
6	2	-8	51.0	52.4	14	2	-1	16.0	15.9	3	3	-1	25.7	24.9	11	3	3	87.5	-98.9

TABLE 4

(CONTINUED)

H	K	L	Fo	Fc	H	K	L	Fo	Fc	H	K	L	Fo	Fc	H	K	L	Fo	Fc
11	3	4	41.6	38.6	0	4	12	19.8	20.4	8	4	11	20.6	-19.0	3	5	5	59.5	61.3
11	3	5	47.7	51.8	0	4	13	22.7	-24.8	8	4	-1	32.0	22.5	3	5	8	21.0	19.9
11	3	7	22.1	23.9	0	4	14	16.4	17.0	8	4	-2	86.4	79.7	3	5	9	20.7	-15.8
11	3	8	30.2	-29.7	0	4	15	9.5	-14.7	8	4	-4	12.0	-12.2	3	5	10	14.0	13.8
11	3	-1	38.0	35.8	2	4	0	11.5	-11.1	8	4	-5	39.9	36.5	3	5	11	18.4	-19.4
11	3	-2	27.7	24.6	2	4	1	85.9	89.9	8	4	-6	25.4	-22.2	3	5	12	30.1	26.6
11	3	-3	58.3	-62.6	2	4	2	22.3	22.4	8	4	-7	18.6	-16.6	3	5	-1	66.2	62.6
11	3	-4	30.7	-31.6	2	4	4	77.7	-77.4	8	4	-9	37.3	-40.3	3	5	-2	69.0	69.3
11	3	-5	49.2	49.3	2	4	5	15.9	9.0	8	4	-10	35.3	33.9	3	5	-5	30.1	-31.7
11	3	-7	78.8	86.5	2	4	6	32.4	30.2	8	4	-11	70.4	73.6	3	5	-6	21.5	-19.3
11	3	-8	29.0	27.2	2	4	7	26.3	-24.9	8	4	-14	25.9	-27.7	3	5	-7	54.2	55.8
11	3	-9	59.1	-58.1	2	4	8	44.0	45.9	8	4	-15	30.8	-30.3	3	5	-10	25.7	-26.0
11	3	-10	27.3	-26.5	2	4	9	14.4	-14.2	10	4	0	55.5	-50.9	3	5	-11	25.4	-25.7
11	3	-11	21.3	-22.9	2	4	10	38.4	-37.1	10	4	1	14.1	-11.0	5	5	2	30.0	26.0
11	3	-12	42.1	-45.8	2	4	11	24.6	21.5	10	4	2	35.2	-35.4	5	5	3	63.8	-66.2
11	3	-14	19.4	17.2	2	4	13	38.0	37.9	10	4	3	55.2	59.2	5	5	4	23.8	-24.3
11	3	-15	17.8	18.6	2	4	15	34.5	-37.8	10	4	4	20.5	16.2	5	5	7	21.0	23.3
11	3	-17	31.0	-34.9	2	4	-1	40.9	-38.2	10	4	6	19.5	17.5	5	5	10	27.9	-11.1
13	3	0	27.4	27.3	2	4	-2	139.4	-146.2	10	4	7	22.5	-26.3	5	5	11	28.7	-25.2
13	3	1	32.4	34.5	2	4	-3	46.9	-40.4	10	4	8	35.3	-31.1	5	5	12	43.5	37.5
13	3	2	38.4	-41.1	2	4	-4	30.7	24.0	10	4	-1	83.0	-79.4	5	5	-1	52.1	44.6
13	3	3	20.6	-18.9	2	4	-5	43.3	-36.9	10	4	-3	18.9	17.6	5	5	-3	74.4	-63.8
13	3	4	11.5	-13.4	2	4	-6	45.6	44.9	10	4	-5	13.5	15.6	5	5	-4	22.7	-21.2
13	3	5	45.3	-46.4	2	4	-7	91.3	92.9	10	4	-6	43.4	-36.9	5	5	-7	57.5	63.3
13	3	6	28.1	29.5	2	4	-8	32.9	-30.1	10	4	-8	28.4	30.8	5	5	-8	63.4	73.9
13	3	7	30.9	33.0	2	4	-9	60.5	-63.5	10	4	-9	40.8	-42.4	5	5	-9	41.4	-39.6
13	3	8	12.2	-11.1	2	4	-10	40.4	-42.5	10	4	-10	29.1	28.9	5	5	-14	29.5	30.1
13	3	-1	21.2	20.1	2	4	-11	25.2	-24.0	10	4	-11	14.4	18.7	5	5	-15	16.6	-17.3
13	3	-2	50.2	51.3	2	4	-12	20.3	24.8	12	4	4	30.3	28.9	7	5	0	68.1	64.1
13	3	-3	91.2	-109.3	2	4	-14	12.5	14.0	12	4	6	46.3	46.6	7	5	1	70.3	72.7
13	3	-4	29.7	-28.3	4	4	0	57.3	56.6	12	4	8	17.9	-20.5	7	5	2	36.7	-31.3
13	3	-5	44.5	47.6	4	4	1	73.0	66.2	12	4	-3	95.5	89.6	7	5	3	24.8	-25.0
13	3	-6	27.2	29.3	4	4	2	109.1	120.9	12	4	-5	35.2	-35.3	7	5	4	29.3	-26.9
13	3	-7	43.2	43.2	4	4	3	58.1	-50.5	12	4	-6	14.4	-4.8	7	5	5	33.2	-31.3
13	3	-8	24.5	25.6	4	4	4	44.2	-42.3	12	4	-7	41.0	-38.0	7	5	6	29.5	29.5
13	3	-9	38.8	-39.4	4	4	5	52.2	-48.3	12	4	-8	20.5	18.3	7	5	7	43.0	41.0
13	3	-11	17.0	15.9	4	4	6	26.6	-29.0	12	4	-9	29.0	32.0	7	5	-1	33.6	-25.7
13	3	-13	15.9	18.2	4	4	7	53.2	51.6	12	4	-12	35.7	-38.3	7	5	-4	33.8	-29.3
13	3	-15	13.3	-15.5	4	4	8	35.3	34.4	12	4	-14	28.4	27.9	7	5	-5	26.3	26.0
13	3	-16	18.0	-16.1	4	4	9	25.2	-23.3	14	4	1	23.3	-19.7	7	5	-6	71.3	-77.4
13	3	-17	17.7	18.2	4	4	10	20.1	26.2	14	4	2	28.9	-25.0	7	5	-7	19.9	21.8
15	3	1	50.8	47.4	4	4	12	34.2	-33.4	14	4	5	31.0	34.6	7	5	-8	14.5	15.6
15	3	3	14.5	15.8	4	4	14	12.7	12.7	14	4	6	15.6	16.3	7	5	-9	33.0	-35.4
15	3	4	22.9	-21.3	4	4	-1	27.4	-22.9	14	4	-3	14.3	12.9	7	5	-11	26.2	19.7
15	3	5	41.8	-42.9	4	4	-2	37.8	-31.0	14	4	-4	24.9	-26.0	9	5	0	49.8	53.9
15	3	6	18.5	20.3	4	4	-3	56.1	47.2	14	4	-6	20.3	21.1	9	5	1	41.3	41.2
15	3	-1	37.7	-37.5	4	4	-4	58.1	44.1	14	4	-10	33.2	-33.8	9	5	5	53.9	-50.9
15	3	-2	40.0	-40.5	4	4	-5	32.8	26.3	14	4	-11	26.1	-26.9	9	5	-1	40.1	-41.8
15	3	-3	17.2	17.0	4	4	-6	27.0	21.5	14	4	-14	31.9	35.6	9	5	-2	38.5	-37.7
15	3	-4	17.2	-15.9	4	4	-7	45.5	-40.2	14	4	-15	16.5	18.1	9	5	-4	24.4	-25.3
15	3	-5	12.2	-8.9	4	4	-8	65.3	-69.8	16	4	0	32.8	30.7	9	5	-6	51.9	62.3
15	3	-6	38.5	36.5	4	4	-10	20.0	20.2	16	4	3	37.3	-33.2	9	5	-7	35.8	-38.1
15	3	-9	49.1	-44.2	4	4	-13	31.2	33.4	16	4	-1	44.7	37.5	9	5	-8	25.6	-22.7
15	3	-10	20.2	-20.6	4	4	-17	13.3	-25.8	16	4	-4	26.1	-23.9	9	5	-9	21.0	21.6
15	3	-11	33.9	30.5	6	4	1	55.7	55.0	16	4	-5	13.1	-17.5	11	5	0	21.0	22.3
15	3	-13	20.2	16.3	6	4	2	11.7	15.7	16	4	-6	41.3	42.2	11	5	3	24.6	26.0
15	3	-15	16.0	-14.0	6	4	3	12.4	9.8	16	4	-10	51.9	-53.1	11	5	-1	14.8	-14.7
17	3	0	21.7	17.8	6	4	4	13.0	-6.7	16	4	-11	29.7	29.5	11	5	-2	25.7	-26.9
17	3	1	25.5	25.6	6	4	5	19.4	19.7	16	4	-13	18.2	-18.4	11	5	-3	25.6	26.7
17	3	2	18.2	16.2	6	4	6	86.4	-94.8	18	4	-6	25.5	26.1	11	5	-7	25.7	-26.7
17	3	3	29.2	33.1	6	4	7	41.0	-39.9	18	4	-7	10.3	13.4	11	5	-8	44.3	-43.9
17	3	4	19.9	-25.5	6	4	9	14.0	18.0	18	4	-8	20.1	-18.2	11	5	-12	38.9	37.3
17	3	-1	28.8	-28.7	6	4	10	26.4	28.8	1	5	2	23.1	-22.7	11	5	-13	36.6	-31.2
17	3	-2	10.6	10.7	6	4	12	31.6	-35.2	1	5	3	56.8	-55.1	11	5	-14	48.8	-46.1
17	3	-3	15.3	14.6	6	4	13	15.4	15.4	1	5	4	75.5	78.7	13	5	0	56.7	-58.7
17	3	-7	45.5	-38.6	6	4	-1	106.5	-94.5	1	5	5	44.0	45.9	13	5	1	23.4	-24.9
17	3	-9	26.0	21.5	6	4	-2	27.6	20.5	1	5	6	53.7	-54.2	13	5	2	40.9	43.2
17	3	-10	20.5	18.8	6	4	-3	27.0	-22.9	1	5	7	19.9	15.8	13	5	-1	14.2	13.6
19	3	-1	13.5	-14.1	6	4	-4	18.3	15.6	1	5	8	46.2	-52.8	13	5	-3	14.5	10.6
19	3	-3	25.6	27.2	6	4	-5	46.3	42.1	1	5	9	29.7	-34.9	13	5	-4	46.0	48.9
19	3	-4	11.9	-9.9	6	4	-6	39.7	-35.8	1	5	10	29.3	28.9	13	5	-5	29.1	-28.2
19	3	-5	15.0	10.4	6	4	-7	21.5	16.8	1	5	13	22.2	18.5	13	5	-6	28.9	28.3
19	3	-7	28.9	-29.0	6	4	-8	41.4	-36.5	1	5	-3	17.4	17.3	13	5	-9	27.5	24.7
19	3	-8	8.5	-11.1	6	4	-9	23.8	-25.5	1	5	-4	36.6	32.3	13	5	-13	16.4	-18.7
19	3	-10	19.2	-18.1	6	4	-10	20.1	21.6	1	5	-5	60.5	-63.2	15	5	0	19.9	-21.9
19	3	-11	16.0	14.2	6	4	-14	22.7	-24.2	1	5	-6	43.6	39.0	15	5	1	10.6	-13.6
0	4	1	75.9	-101.4	6	4	-16	22.0	21.6	1	5	-9	46.6	48.6	15	5	-3	12.8	15.5
0	4	4	41.9	-39.0	8	4	0	32.8	-27.7	1	5	-11	25.1	-25.1	15	5	-4	18.4	20.4
0	4	5	39.0	31.4	8	4	1	28.6	-25.2	1	5	-12	36.0	-35.6	15	5	-5	26.1	-29.7
0	4	6	106.0	103.6	8	4	2	26.5	22.7	3	5	1	22.7	-17.1	15	5	-6	45.0	-48.7
0	4	7	35.1	-33.2	8	4	4	34.7	35.7	3	5	2	75.9	-75.6	15	5	-7	28.7	30.2
0	4	8	29.8	28.9	8	4	6	32.5	-35.5	3	5	3	37.6	-34.0	15	5	-8	21.6	21.8
0	4	9	28.0	24.5	8	4	9	25.4	28.5	3	5	4	21.4	16.3	15	5	-11	30.2	-31.2
0	4	10	35.4	-42.3	8	4	10	33.7	36.4										

Discussion

The overall structure was described by MacArthur and Beevers (1957). This refinement has produced shifts of 0·02 - 0·04 Å from the co-ordinates obtained by Cruickshank (1964), with a larger shift of about 0·15 Å for the water molecule, W(1). A projection of the structure down the b-axis is shown in Figurel, with the Na - O and P - O bonds indicated.

The sodium co-ordination. The bond lengths and angles at the sodium atoms are given in Table 5. The sodium - oxygen bond lengths have estimated standard deviations of 0·007 Å, and the O - Na - O angles have standard deviations of 0·2°. The mean Na - O bond length in the Na(1) octahedron is 2·48 Å, and in the Na(2) octahedron, 2·45 Å. The two Na(1) - W(3) bonds are rather long. This is probably due to the fact that the water molecule W(3) is bonded to five other atoms (three sodiums and two hydrogens), whilst all other atoms co-ordinated to sodium form only four bonds. The water molecules W(1), W(2), and W(4) are each co-ordinated to two sodiums, whilst W(5) is co-ordinated to one sodium and is also the acceptor of a hydrogen bond from W(3)

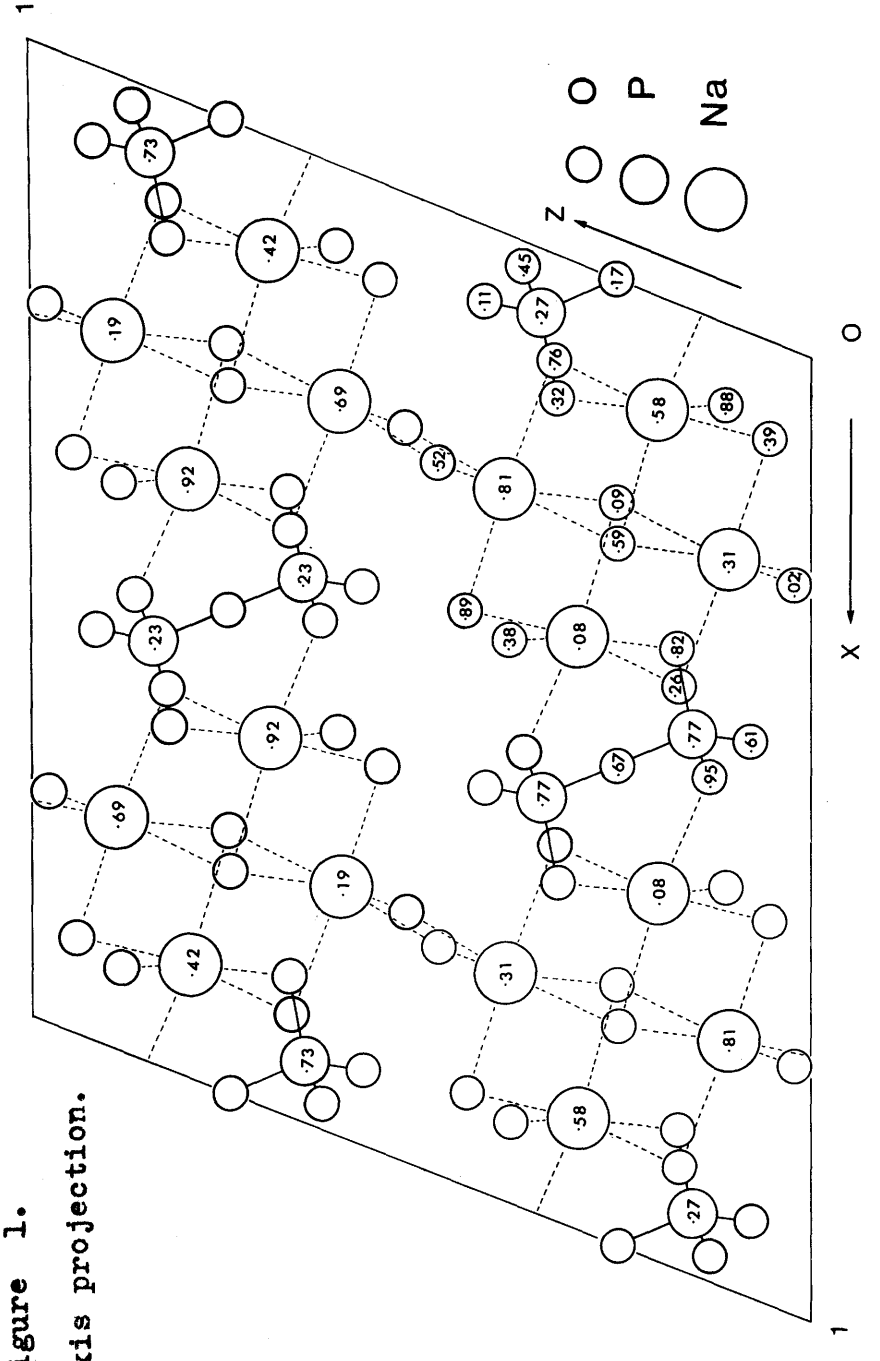

Figure 1.
b-axis projection.

TABLE 5

BOND LENGTHS AND ANGLES AT THE SODIUM ATOMS

BOND			ANGSTROMS
Na(1)	-	W(1)	2.292
Na(1)	-	W(2)	2.353
Na(1)	-	W(2)*	2.377
Na(1)	-	W(4)	2.405
Na(1)	-	W(3)	2.705
Na(1)	-	W(3)*	2.772

BOND			ANGSTROMS
Na(2)	-	W(4)	2.360
Na(2)	-	W(5)	2.415
Na(2)	-	O(2)	2.416
Na(2)	-	W(3)	2.457
Na(2)	-	W(1)	2.479
Na(2)	-	O(4)	2.554

ANGLE					DEGREES
W(1)	-	Na(1)	-	W(2)	103.4
W(1)	-	Na(1)	-	W(2)*	91.7
W(1)	-	Na(1)	-	W(4)	172.0
W(1)	-	Na(1)	-	W(3)	92.3
W(1)	-	Na(1)	-	W(3)*	87.2
W(2)	-	Na(1)	-	W(2)*	88.6
W(2)	-	Na(1)	-	W(4)	84.3
W(2)	-	Na(1)	-	W(3)	87.5
W(2)	-	Na(1)	-	W(3)*	164.6
W(2)*	-	Na(1)	-	W(4)	86.2
W(2)*	-	Na(1)	-	W(3)	175.0
W(2)*	-	Na(1)	-	W(3)*	102.4
W(4)	-	Na(1)	-	W(3)	90.3
W(4)	-	Na(1)	-	W(3)*	85.7
W(3)	-	Na(1)	-	W(3)*	80.8

ANGLE					DEGREES
W(4)	-	Na(2)	-	W(5)	85.2
W(4)	-	Na(2)	-	O(2)	101.7
W(4)	-	Na(2)	-	W(3)	97.8
W(4)	-	Na(2)	-	W(1)	171.6
W(4)	-	Na(2)	-	O(4)	79.5
W(5)	-	Na(2)	-	O(2)	97.2
W(5)	-	Na(2)	-	W(3)	99.3
W(5)	-	Na(2)	-	W(1)	94.4
W(5)	-	Na(2)	-	O(4)	164.7
O(2)	-	Na(2)	-	W(3)	155.4
O(2)	-	Na(2)	-	W(1)	70.0
O(2)	-	Na(2)	-	O(4)	85.4
W(3)	-	Na(2)	-	W(1)	90.6
W(3)	-	Na(2)	-	O(4)	83.5
W(1)	-	Na(2)	-	O(4)	100.6

The pyrophosphate group. The dimensions of the pyrophosphate group are given in Table 6. The estimated standard deviations are 0·005 Å for the P - O bond lengths, 0·6° for the P - O - P angle, and 0·3° for the O - P - O angles. As noted by Cruickshank (1964), the temperature factors for the oxygen atoms are higher than those for phosphorus, and some correction of the bond lengths to allow for the rotational motion of the group is necessary. The temperature factors of the atoms of the group, referred to inertial axes, are given in Table 7. Axis 1 is the axis of minimum inertia and axis 2 is that of maximum inertia. Axis 3 coincides with the crystallographic two-fold axis. The values of these temperature factors do not seem to be consistent with a rigid body vibration of the whole P_2O_7 group, but suggest that the two PO_4 tetrahedra vibrate individually as rigid bodies. The phosphorus atom shows approximately isotropic vibrations, but the oxygens are quite anisotropic. The bridge oxygen, O(1), has a large vibration amplitude normal to the P - O - P plane, suggesting that there is a vibration in which "folding" of the group along the two-fold axis occurs. The temperature factors of the terminal oxygens also suggest a vibration of this kind. In addition, the three terminal oxygens show large vibrations normal to the

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TABLE 6

DIMENSIONS OF THE PYROPHOSPHATE GROUP

BOND	ANGSTROMS	ANGLE	DEGREES
P - O(1)	1.612	P - O(1) - P*	130.2
		O(1) - P - O(2)	108.9
P - O(2)	1.510	O(1) - P - O(3)	101.8
		O(1) - P - O(4)	106.6
P - O(3)	1.503	O(2) - P - O(3)	112.8
		O(2) - P - O(4)	111.1
P - O(4)	1.526	O(3) - P - O(4)	115.0

TABLE 7

TEMPERATURE FACTORS OF THE ATOMS OF THE PYROPHOSPHATE GROUP REFERRED TO INERTIAL AXES

ATOM	U11	U22	U33	U23	U31	U12
P	0.0134	0.0175	0.0145	0.0017	-0.0018	0.0008
O(1)	0.0173	0.0496	0.0129	0	0	0.0017
O(2)	0.0288	0.0282	0.0142	0.0044	0.0016	0.0044
O(3)	0.0256	0.0359	0.0346	-0.0066	-0.0078	-0.0066
O(4)	0.0357	0.0193	0.0321	-0.0003	0.0092	0.0040

P - O(1) bond and normal also to the separate terminal P - O bonds, suggesting a rotational oscillation of the PO_3 group about the axis of the bridge bond. Separate vibrational corrections need to be applied for each of these types of motion. Since the bridge oxygen is constrained by symmetry to move in a straight line midway between the two phosphorus atoms, no correction is necessary to the P - O(1) length. The rotational oscillation about the P - O(1) bond requires a correction of about 0·005 Å to the three terminal bonds. The folding vibration requires a further correction of about 0·007 Å to the P - O(4) bond, and corrections of about 0·004 Å to P - O(2) and P - O(3). The corrected bond lengths are then 1·519 for P - O(2), 1·512 for P - O(3), and 1·537 Å for P - O(4).

The mean terminal P - O bond length is therefore 1·523 Å, and the bridge bond length is 1·612 Å. The difference of about 0·1 Å therefore falls midway between the 0·2 Å difference found in S_2O_7 (Lynton and Truter, 1960) and the zero difference found in Si_2O_7 in the previous chapter.

Two other pyrophosphate structures have been determined recently, however, in which the dimensions of the pyrophosphate group are rather different.

In β-$Mg_2P_2O_7$ and in β-$Zn_2P_2O_7$ (Calvo, 1965) the terminal bonds are of mean length 1·539 Å and 1·555 Å respectively, and the bridge bonds are 1·557 Å and 1·569 Å respectively. In both of these structures, however, the P - O - P angle is 180°, compared with 130° in sodium pyrophosphate, and the greater angle would be expected to make the π-bond orders, and therefore the bond lengths, more nearly equal. There is also considerable uncertainty as to what rotational corrections are necessary for the magnesium and zinc salts.

The hydrogen bonding. Table 8 gives the hydrogen bond lengths and angles. The water molecules W(1) and W(2) each form two hydrogen bonds of length 2·7 - 2·8 Å. W(3), W(4), and W(5) each form one hydrogen bond of about this length, and a second longer bond of 2·9 - 3·0 Å. Two of these longer bonds are to O(3), which is bonded to phosphorus, and is also the acceptor of a third hydrogen bond. The other long hydrogen bond is the only one between two water molecules.

The standard deviations of the hydrogen atom co-ordinates are 0·1 to 0·2 Å. They are so high that the W - H and O - H distances are not very meaningful. H(42), in particular, with a W - H distance of 0·66 Å, is obviously very poorly located.

TABLE 8 HYDROGEN BOND LENGTHS AND ANGLES

BOND	ANGSTROMS	BOND	ANGSTROMS	BOND	ANGSTROMS	ANGLE	DEGREES
W(1)-O(2)*	2.786	W(1)-H(11)	0.97	H(11)-O(2)*	1.87	W(1)-H(11)-O(2)*	156
W(1)-O(2)	2.812	W(1)-H(12)	0.72	H(12)-O(2)	2.10	W(1)-H(12)-O(2)	168
						H(11)-W(1)-H(12)	85
W(2)-O(3)	2.770	W(2)-H(21)	0.98	H(21)-O(3)	1.87	W(2)-H(21)-O(3)	152
W(2)-O(4)	2.737	W(2)-H(22)	1.03	H(22)-O(4)	1.94	W(2)-H(22)-O(4)	133
						H(21)-W(2)-H(22)	112
W(3)-O(4)	2.708	W(3)-H(31)	0.92	H(31)-O(4)	1.85	W(3)-H(31)-O(4)	153
W(3)-W(5)	2.934	W(3)-H(32)	1.14	H(32)-W(5)	1.80	W(3)-H(32)-W(5)	171
						H(31)-W(3)-H(32)	92
W(4)-O(2)	2.793	W(4)-H(41)	1.05	H(41)-O(2)	1.79	W(4)-H(41)-O(2)	159
W(4)-O(3)	2.919	W(4)-H(42)	0.66	H(42)-O(3)	2.29	W(4)-H(42)-O(3)	159
						H(41)-W(4)-H(42)	87
W(5)-O(3)	3.059	W(5)-H(51)	0.83	H(51)-O(3)	2.31	W(5)-H(51)-O(3)	151
W(5)-O(3)*	2.783	W(5)-H(52)	1.18	H(52)-O(3)*	1.65	W(5)-H(52)-O(3)*	160
						H(51)-W(5)-H(52)	93

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Chapter 6

The Crystal Structure of Dipotassium Ethyl Phosphate Tetrahydrate

The need for an accurate analysis of a structure containing the $[PO_3.OR]^{2-}$ ion was pointed out by Cruickshank (1961) in his discussion of π-bonding in phosphate ions. On the basis of expected π-bond orders a length of 1·62 - 1·63 Å was predicted for the P -O(R) bond. This analysis was undertaken in the hope of obtaining accurate dimensions for the ethyl phosphate anion.

Preparation of Crystals

A sample of $K_2EtPO_4.H_2O$ was kindly supplied by Dr. Maryon Dougill. This material was obtained by drying at 100° the product which crystallised from water, and was not suitable for single crystal work. A saturated aqueous solution of the salt was evaporated at room temperature over KOH pellets in a desicator. Large irregular, deliquescent crystals were obtained. For the X-ray measurements small fragments of these crystals were removed from the solution and sealed in capillaries.

Space Group and Cell Dimensions

From Weissenberg and precession photographs the crystals were seen to be orthorhombic, with systematic absences as follows:-

hkl: h+1 odd

h0l: h odd, l odd.

hk0: h odd, k odd.

0kl: l odd.

This indicates that the space group is B2cb (No. 41) or Bmab(No. 64). The cell dimensions, measured from zero - layer precession photographs, were a = 10·03 ± 0·01 Å, b = 20·65 ± 0·02 Å, c = 10·47 ± 0·01 Å. The density determined by flotation in a CCl_4 - CH_2I_2 mixture, was 1·67. Eight molecules of $K_2EtPO_4.4H_2O$ per cell give a calculated density of 1·680. The crystals were therefore those of the tetrahydrate.

A long - exposure rotation photograph, taken with the crystal rotating about the [1 0 1] axis, showed some weak reflections on the h+1 odd rows, indicating that the B face-centring was imperfect, and that the true lattice is a primitive one. As these extra reflections were extremely weak, they were ignored in the first stages of the structure determination, and the structure was treated as if it had a B lattice.

Collection of the Data

E qui-inclination Weissenberg photographs were taken with the crystal oscillated about the [1 0 1] axis. Copper Kα radiation was used, and multiple-film

photographs of layers h+1 = 0, 2, 4 and 6 were obtained. Intensities were estimated visually and the layers were correlated by means of the common reflections. Lorentz and polarisation factors were applied using a DEUCE computer programme written by J.G. Sime, giving a set of 623 independent structure amplitudes on a common scale.

Solution of the Pseudo-symmetric Structure

A sharpened 3-dimensional Patterson synthesis was computed, using the Fourier programme written by J.S. Rollett for the DEUCE computer. In interpreting the Patterson map it was initially assumed that the structure had the non-centrosymmetric space group B2cb. In this space group vectors between non-symmetry related atoms occur in sets of four with co-ordinates $(\Delta x, \Delta y, \Delta z)$, $(\Delta x, \sum y, \sum z)$, $(\Delta x, \frac{1}{2} - \Delta y, \frac{1}{2} - \sum z)$, and $(\Delta x, \frac{1}{2} - \sum y, \frac{1}{2} - \Delta z)$, where Δ and $\sum$ indicate the difference and sum respectively of corresponding co-ordinates of the two atoms. If we put $\Delta x = 0$ and $\sum x = 2x$, etc., we get the Harker peaks $(0, 0, 0)$, $(0, 2y, 2z)$, $(0, \frac{1}{2}, \frac{1}{2} - 2z)$ and $(0, \frac{1}{2} - 2y, \frac{1}{2})$. B2cb is a polar space group, with an arbitrary origin in the x-direction, so that the x-co-ordinate of any one atom may be chosen arbitrarily. By inspection of a list of the stronger peaks on the Patterson map, a set of four general vectors between a pair of independent atoms was readily recognised. This led to co-ordinates

for these two atoms of (0, 0·417, 0·392) and (0, 0·175, 0·172), which were confirmed by the presence of the expected Harker peaks. Thus two of the three heavier atoms have the same x-co-ordinate, suggesting that they may be in special positions of the higher symmetry space group Bmab, with the two atoms lying on the mirror planes. If the space group is Bmab the third heavy atom must also be in a special position. With one exception, the remaining strong peaks on the Patterson map could be interpreted on this assumption, with the third heavy atom on a 2-fold axis at $(\frac{1}{4}, \frac{1}{4}, 0{\cdot}483)$. The one strong peak on the Patterson map that remained unaccounted for was only 1·5 Å from the origin, too short a distance for it to be a vector between heavy atoms. When the remainder of the atoms had been located it became clear that this peak arose from the superposition of four P-O vectors.

For an initial structure factor calculation the above co-ordinates for the three heavy atoms were used. All three were assumed to be K^+, with isotropic temperature factors of B = 2·5 $Å^2$. This calculation gave an R value ($R = \sum||KF_o| - |Fc|| / \sum|KFo|$) of 0·42.

Using the phases so calculated, an Fo Fourier synthesis revealed all other atoms except the two carbons; the oxygen positions indicated which of the three heavy atoms was phosphorus. A structure factor calculation then gave an R value of 0·24, and a second Fourier synthesis then showed the carbon atom positions. A structure factor calculation using all atoms then gave an R value of 0·18.

Least-squares refinement in space group Bmab

The atomic co-ordinates, anisotropic temperature factors, and an overall scale factor were refined, using the block diagonal least-squares programme written by J.S. Rollett for the DEUCE computer. The weighting scheme used was $w = 1$ for $|Fo| \leq 30$, $w = |Fo|^2/30^2$ for $|Fo| > 30$. Five cycles of refinement reduced the residual to R = 0·119, giving the atomic parameters listed in Table 1.

Atom K(1) lies on a 2-fold axis in this space group, atoms K(2), P, O(1), O(2), C(1), and C(2), are on the mirror plane, and O(3), O(4) and O(5) are in general positions. The effect of constraining certain atoms to lie on the mirror plane is shown by the high values of U_{11} for some of these atoms, and by the very short C-C single bond distance of 1·36 Å.

TABLE 1 ATOMIC PARAMETERS FROM THE PSEUDO-SYMMETRIC REFINEMENT

ATOM	x	y	z	U11	U22	U33	2U23	2U31	2U12
K(1)	1/4	1/4	0.4844	0.056	0.038	0.010	0	0	0.035
K(2)	0	0.4150	0.3979	0.035	0.023	0.019	-0.002	0	0
P	0	0.1747	0.1712	0.034	0.017	0.004	0.002	0	0
O(1)	0	0.1697	0.3206	0.066	0.040	0.003	0.001	0	0
O(2)	0	0.2478	0.1464	0.045	0.014	0.026	0.004	0	0
O(3)	0.1255	0.1424	0.1233	0.046	0.029	0.023	-0.006	0.000	0.002
O(4)	0.1888	0.0147	0.1315	0.043	0.039	0.051	-0.012	0.015	0.001
O(5)	0.1671	0.3271	0.2857	0.042	0.043	0.013	-0.006	0.011	0.003
C(1)	0	0.1046	0.3818	0.175	0.024	0.041	0.026	0	0
C(2)	0	0.1004	0.5119	0.238	0.065	0.011	0.001	0	0

Determination of the True Space Group

Since the h+l odd reflections are extremely weak, and the refinement assuming a higher symmetry led to a relatively low R value, the displacements of the true structure from the Bmab structure cannot be very great. The full symmetry elements of this space group are B, $2+2_1/m+c$, $2+2_1/a+c$, $2_1+2_1/b+n$. The weak reflections require that the lattice must become primitive, but there seems to be no reason for reducing the point group symmetry below m m m. We therefore have to make a choice between the 8 sub-groups of Bmab having point group m m m. These are Pman (No. 53), Pccb (No. 54), Pmcb (No. 55), Pccn (No. 56), Pmab (No. 57), Pcan(No. 60), Pcab (No. 61), and Pmcn (No. 62). The distinction between these 8 possibilities depends on the determination of which of the mirror or glide planes are present in the true space group, and which are only pseudo--symmetry elements.

A long exposure precession photograph of the h0l reciprocal lattice layer showed two very weak reflections, 104 and 108. These violate the requirements of the a-glide plane, and indicate that the true symmetry element normal to the y-axis is a c-glide.

A long exposure Weissenberg film of the hK0 layer showed 6 very weak reflections, 170, 350, 370, 5 15 0,

9 5 0, and 9 7 0. These indicate that the b-glide is a pseudo-symmetry element.

On a photograph of the 0kl layer no additional weak reflections were observable. This, together with the large U_{11} vibration parameters obtained for some of the light atoms on the mirror plane, suggests that this mirror plane is a pseudo-symmetry element.

If these conclusions are correct the true space group must be Pccn (No. 56). The true symmetry elements and the pseudo-symmetry elements are shown in Figure 1.

The Structure in Space Group Pccn

Long exposure Weissenberg photographs of layers hK0 to hK3 were taken. On these photographs only 12 of the weak class of reflections were observable. Two additional weak reflections on the h0l photograph gave a total of only 14 reflections, which is clearly insufficient to determine the true structure. It was therefore necessary to make use of the additional information provided by the strong class of reflections.

For the strong class of reflections, the values of F_c depend on the magnitudes of the displacements from the pseudo-symmetric structure, but are independent of the signs of these displacements. A least-squares refinement in the true space group, but using the

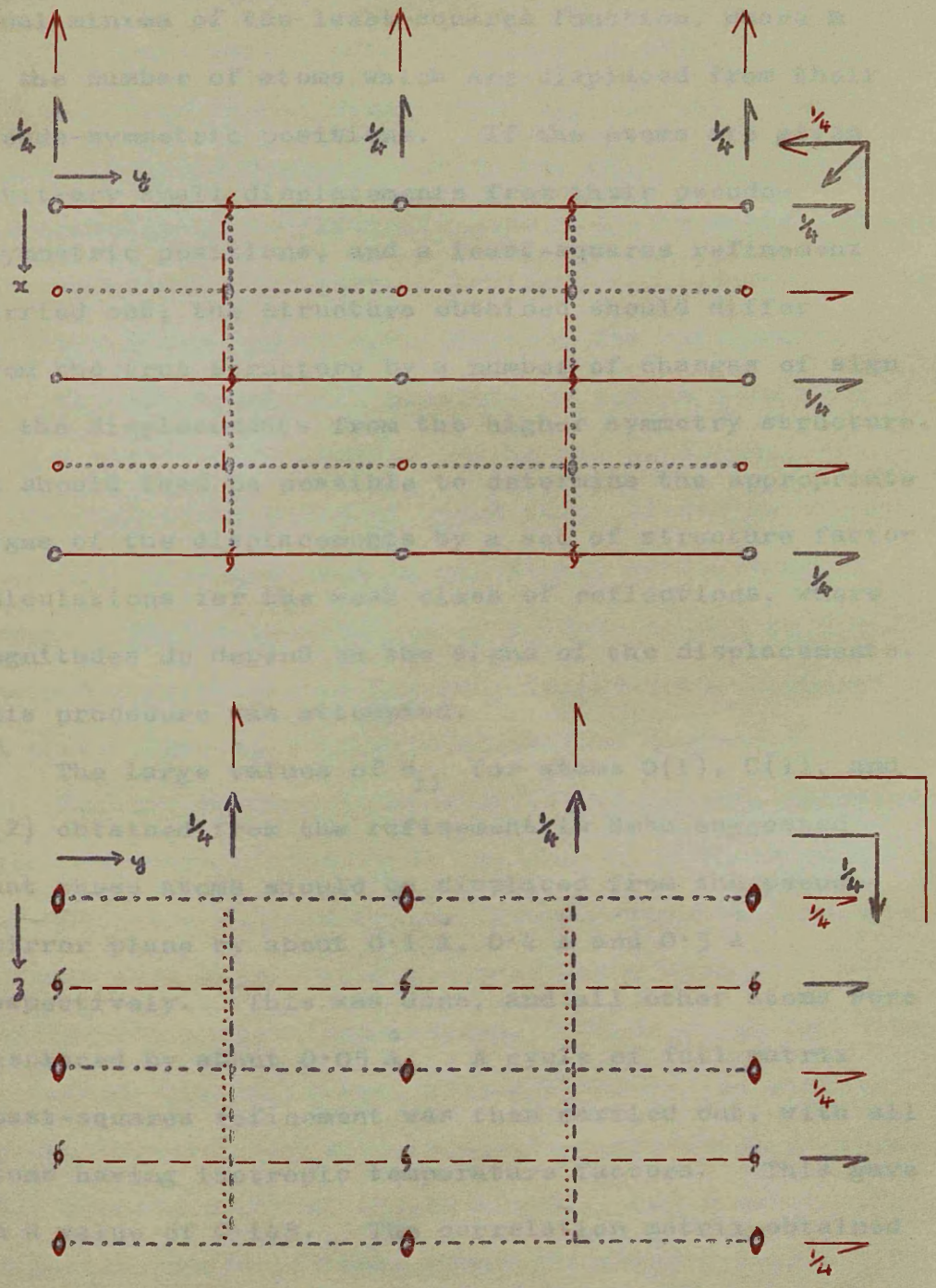

Figure 1. Relationship between the two space groups. True symmetry elements in black. Pseudo-symmetry elements in red.

strong class of reflections only, could lead to 2^{n-1} equal minima of the least-squares function, where n is the number of atoms which are displaced from their pseudo-symmetric positions. If the atoms are given arbitrary small displacements from their pseudo--symmetric positions, and a least-squares refinement carried out, the structure obtained should differ from the true structure by a number of changes of sign of the displacements from the higher symmetry structure. It should then be possible to determine the appropriate signs of the displacements by a set of structure factor calculations for the weak class of reflections, where magnitudes do depend on the signs of the displacements. This procedure was attempted.

The large values of U_{11} for atoms O(1), C(1), and C(2) obtained from the refinement in Bmab suggested that these atoms should be displaced from the pseudo--mirror plane by about 0·1 Å, 0·4 Å and 0·5 Å respectively. This was done, and all other atoms were displaced by about 0·05 Å. A cycle of full matrix least-squares refinement was then carried out, with all atoms having isotropic temperature factors. This gave an R value of 0·148. The correlation matrix obtained

from this cycle showed two notable features. Atoms which had been displaced slightly from the falso mirror--plane showed correlation coefficients of 0·3 to 0·6 between their x co-ordinates and U_{11} values. Pairs of atoms which had been related by the false mirror-plane had correlation coefficients very close to unity between corresponding parameters. Furthermore, extremely large shifts for such pairs were given by the refinement.

It was clearly not possible to refine each atom of such a pair independently, and in all subsequent refinement these pairs of atoms were refined as though they were a single atom in the higher symmetry space group. The correlation co-efficients of 0·3 to 0·6 for the other atoms seemed unlikely to prevent refinement of these atoms to a true least-squares minimum.

For the further least-squares refinement, therefore, the atoms were divided into two groups. Those which were in pairs related by the false mirror-plane were refined as a single atom for each pair, with anisotropic temperature factors. Those which had been displaced from their special positions on the mirror--plane were refined with isotropic temperature factors. This procedure worked satisfactorily, and 6 cycles of refinement produced convergence, reducing R from 0·148

to 0·118, a value very little lower than that obtained from the fully anisotropic refinement in the higher symmetry space group. In a final cycle the two carbon atoms were allowed to become anisotropic also, but this had very little effect reducing the residual to 0·116, The displacements from the mirror plane obtained were 0·10 Å for K(2), 0·11 Å for P, 0·19 Å for O(1), 0·16 Å for O(2), 0·33 Å for C(1), and 0·42 Å for C(2).

The next step was to use these new atomic parameters, to calculate structure factors for the weak class of reflections. Since only those atoms which were displaced from their pseudo-symmetric positions contribute to this class of reflections, six sets of structure factors were calculated, giving the contributions of each of the six displaced atoms to the weak structure factors.

Combinations of the six contributions with various sign permutations were tried in an attempt to explain the observed and unobserved reflections in the weak class. No satisfactory agreement could be obtained, although the calculated valueswere of about the right order of magnitude. This failure is probably due to the fact that the contributions of the atoms which were not displaced from their pseudo-symmetric positions cannot be obtained. One is forced to the conclusion that the accuracy of measurement of the strong class

of reflections, and the number observable in the weak class of reflections, are inadequate to determine completely the true structure. More accurate data for the strong class would permit a more precise determination of the displacements of those atoms near the false mirror-plane, and more extensive data for the weak class would allow refinement of the other atoms in the true space group.

The final co-ordinates and their estimated standard deviations are given in Table 2. Table 3 gives the temperature factors, and the observed and calculated structure factors are listed in Table 4.

Description of the Structure

In the following discussion the pseudo-symmetric structure has been assumed in calculating bond lengths and angles. The lower symmetry is only considered in those parts of the structure where deviations from the higher symmetry are indicated by the calculated dimensions. A projection of the structure down the [1 0 0] axis is shown in Figure 2. Only the P-O, C-O, and C-C bonds have been shown. The potassium ions are in layers at $x = 0, \frac{1}{4}, \frac{1}{2}$, and $\frac{3}{4}$, with four potassiums per cell in each layer. The ethyl phosphate ions are in layers at $x = 0$ and $\frac{1}{2}$, with four ethyl phosphate groups per cell in each layer. The four water molecules are independent

TABLE 2

FINAL FRACTIONAL CO-ORDINATES AND ESTIMATED STANDARD DEVIATIONS

ATOM	x	y	z
K(1)	1/4	1/4	0.4842(4)
K(1)*	-1/4	1/4	0.4842(4)
K(2)	±0.0096(14)	0.4143(2)	0.3975(4)
P	±0.0107(14)	0.1749(2)	0.1721(4)
O(1)	±0.0186(27)	0.1696(5)	0.3197(12)
O(2)	±0.0162(28)	0.2481(4)	0.1459(11)
O(3)	0.1254(10)	0.1425(4)	0.1233(8)
O(3)*	-0.1254(10)	0.1425(4)	0.1233(8)
O(4)	0.1878(14)	0.0146(4)	0.1307(10)
O(4)*	-0.1878(14)	0.0146(4)	0.1307(10)
O(5)	0.1653(10)	0.3272(4)	0.2864(8)
O(5)*	-0.1653(10)	0.3272(4)	0.2864(8)
C(1)	±0.0327(26)	0.1055(9)	0.3819(23)
C(2)	±0.0417(29)	0.0998(11)	0.5095(27)

TABLE 3

TEMPERATURE FACTORS
(E.S.D.s GIVEN IN BRACKETS ARE IN UNITS IN THE FOURTH PLACE)

ATOM	U11	U22	U33	2U23	2U31	2U12
K(1)	0.0668(38)	0.0379(17)	0.0134(27)	0	0	0.0477(38)
K(2)	Uiso = 0.0220(12)					
P(1)	Uiso = 0.0136(12)					
O(1)	Uiso = 0.0223(33)					
O(2)	Uiso = 0.0177(32)					
O(3)	0.0325(65)	0.0360(36)	0.0170(51)	-0.0093(61)	0.0038(70)	0.0058(79)
O(4)	0.0607(95)	0.0392(42)	0.0532(77)	-0.0206(85)	0.0080(104)	0.0086(89)
O(5)	0.0284(76)	0.0433(40)	0.0191(56)	-0.0014(62)	0.0012(60)	0.0081(75)
C(1)	Uiso = 0.0289(55)					
C(2)	Uiso = 0.0384(68)					

TABLE 4

OBSERVED AND CALCULATED STRUCTURE FACTORS

H	K	L	Fo	Fc	H	K	L	Fo	Fc	H	K	L	Fo	Fc	H	K	L	Fo	Fc
0	0	4	158.3	-182.1	1	2	1	77.9	-91.0	2	0	6	13.8	-9.6	2	24	2	25.7	-24.6
0	0	6	155.8	126.3	1	2	3	15.1	7.6	2	0	8	81.8	-53.7	2	24	4	63.7	-56.9
0	1	4	56.8	57.6	1	2	5	129.0	120.1	2	1	2	37.0	-43.5	2	25	4	16.9	20.4
0	1	6	139.1	130.2	1	2	7	112.9	-74.3	2	1	4	62.8	63.6	2	26	2	20.9	32.2
0	2	0	149.1	-186.5	1	3	1	33.1	-41.2	2	1	6	98.2	-87.1	3	1	1	47.2	-39.2
0	2	2	30.7	17.5	1	3	3	92.1	91.2	2	1	8	131.8	-100.2	3	1	3	52.8	51.4
0	2	4	161.1	-165.4	1	3	5	25.3	-24.4	2	2	2	171.6	177.8	3	1	7	32.4	-28.5
0	2	6	150.8	-145.0	1	4	1	112.6	144.8	2	2	4	186.3	162.9	3	1	9	21.3	-20.2
0	3	2	121.8	107.5	1	4	3	119.2	105.7	2	2	6	56.0	-37.6	3	2	1	69.4	-70.5
0	3	4	19.1	-9.3	1	4	5	98.8	-82.7	2	2	8	82.3	59.7	3	2	3	162.3	182.0
0	3	6	108.1	-108.2	1	4	7	31.0	21.0	2	3	2	239.3	231.8	3	2	7	154.5	-119.6
0	4	0	57.3	-48.1	1	5	1	17.9	6.9	2	3	4	48.7	52.5	3	2	9	30.1	27.9
0	4	2	115.3	110.7	1	5	3	22.8	-24.6	2	3	6	53.0	-49.4	3	3	1	39.1	-6.4
0	4	4	100.7	107.4	1	5	5	110.4	102.5	2	4	0	194.0	-278.8	3	3	7	67.6	-59.5
0	4	6	111.0	95.7	1	5	7	36.5	30.6	2	4	2	169.0	-139.9	3	3	9	88.2	67.7
0	5	2	67.2	60.5	1	6	1	16.1	11.2	2	4	6	59.5	-52.5	3	4	1	187.4	229.0
0	5	4	99.7	108.2	1	6	3	20.9	21.3	2	4	8	67.2	-58.0	3	4	3	9.5	-3.1
0	5	6	27.3	-32.0	1	6	5	13.0	-3.6	2	5	2	44.6	38.7	3	4	5	51.5	-38.3
0	6	0	58.7	42.8	1	6	7	45.8	-40.6	2	5	4	38.6	-36.9	3	4	7	33.1	27.6
0	6	2	334.7	-306.4	1	7	1	10.0	3.6	2	5	6	41.7	-34.1	3	4	9	64.1	-53.1
0	6	4	58.4	-64.4	1	7	3	22.4	-18.2	2	5	8	76.6	-66.1	3	5	1	57.4	-63.6
0	6	6	46.1	39.0	1	7	5	46.5	34.1	2	6	0	73.1	-57.8	3	5	3	65.9	66.5
0	7	2	120.8	-107.8	1	7	7	38.4	38.7	2	6	2	45.6	30.6	3	5	5	75.9	64.4
0	7	4	98.1	-93.4	1	8	1	125.7	-127.6	2	6	4	145.6	162.2	3	5	7	55.7	47.5
0	7	6	56.2	56.6	1	8	3	125.9	-108.6	2	6	6	153.5	153.1	3	5	9	161.1	-62.1
0	8	0	76.8	86.3	1	8	5	72.4	64.7	2	6	8	68.7	-62.9	3	6	1	45.0	-44.6
0	8	2	196.6	174.0	1	8	7	20.1	15.2	2	7	2	31.7	-35.7	3	6	7	17.0	-11.5
0	8	6	43.1	47.2	1	9	1	39.7	-40.8	2	7	4	41.3	42.5	3	7	1	126.1	-137.4
0	9	2	234.3	-215.1	1	9	3	28.5	26.5	2	7	6	15.5	24.1	3	7	3	99.4	94.1
0	9	6	155.5	154.7	1	9	5	44.2	-43.0	2	7	8	78.3	73.9	3	7	5	82.9	80.2
0	10	0	72.1	-64.9	1	10	1	19.8	-17.4	2	8	0	114.6	-167.6	3	7	9	64.1	-58.0
0	10	2	34.1	-25.9	1	10	3	82.1	-81.7	2	8	2	69.5	-67.5	3	8	1	80.3	-87.2
0	10	4	61.2	-63.4	1	10	5	44.5	-40.2	2	8	4	14.4	-12.9	3	8	3	25.9	21.5
0	10	6	78.5	-78.4	1	10	7	126.6	116.4	2	8	6	79.8	-79.0	3	8	5	15.8	-20.5
0	11	2	27.4	-26.3	1	11	1	45.8	46.8	2	9	2	82.1	-76.0	3	8	7	30.3	-31.6
0	11	4	29.6	-30.0	1	11	3	62.7	-58.5	2	9	4	93.6	-78.6	3	8	9	59.7	52.2
0	11	6	55.6	-55.9	1	11	7	29.6	-28.8	2	9	6	16.4	21.2	3	9	3	13.3	18.3
0	12	0	295.2	316.9	1	12	1	11.6	-12.8	2	10	0	97.0	97.0	3	9	5	28.3	25.7
0	12	4	22.0	-19.9	1	12	3	15.3	15.9	2	10	2	102.6	114.7	3	9	7	53.2	-55.4
0	12	6	76.0	73.7	1	12	5	25.3	28.0	2	10	4	64.6	64.1	3	9	9	55.2	42.2
0	13	2	26.6	23.5	1	12	7	42.3	-33.3	2	10	8	56.5	49.2	3	10	1	118.2	128.8
0	13	4	66.9	56.4	1	13	1	67.8	62.7	2	11	2	74.5	68.9	3	10	3	72.6	-69.7
0	13	6	30.5	28.3	1	13	3	27.4	-26.7	2	11	4	16.7	-19.8	3	10	5	55.7	-52.3
0	14	0	126.1	-135.7	1	13	5	68.9	-70.7	2	11	8	60.3	56.6	3	10	7	82.2	86.2
0	14	2	16.2	13.6	1	14	3	40.6	43.0	2	12	0	76.0	77.3	3	11	1	45.4	46.2
0	14	4	77.4	-79.7	1	14	5	27.0	29.5	2	12	2	72.8	-67.7	3	11	3	46.2	-46.8
0	14	6	110.1	-107.8	1	14	7	64.1	-57.8	2	12	4	141.7	-137.0	3	11	5	88.2	-76.4
0	15	2	23.9	19.7	1	15	3	29.8	28.0	2	12	8	47.4	-40.1	3	12	1	45.4	-47.1
0	15	6	30.1	-29.3	1	15	5	17.9	-13.5	2	13	4	56.9	49.1	3	12	3	13.2	19.0
0	16	0	31.2	26.9	1	15	7	21.1	20.4	2	13	6	59.5	-74.3	3	12	5	17.7	17.4
0	16	4	50.5	50.1	1	16	1	51.9	54.9	2	13	8	80.8	-77.6	3	12	7	18.0	-24.1
0	16	6	76.8	72.4	1	16	3	25.1	24.3	2	14	0	28.1	-27.3	3	13	1	29.6	28.9
0	17	2	47.8	-47.5	1	16	5	34.3	-36.6	2	14	2	87.7	79.7	3	13	3	19.2	22.3
0	17	4	40.4	42.7	1	16	7	20.6	26.6	2	14	4	82.1	80.6	3	13	5	36.1	-29.9
0	17	6	41.9	46.9	1	17	1	31.7	-32.4	2	14	6	44.2	-44.9	3	13	9	32.3	31.2
0	18	0	60.6	-58.4	1	17	3	18.1	-18.5	2	14	8	40.7	42.1	3	14	3	77.7	83.3
0	18	2	73.4	-83.8	1	17	5	78.4	82.4	2	15	2	124.1	127.8	3	14	7	50.0	-59.5
0	18	4	31.2	30.7	1	18	1	40.0	-39.9	2	15	8	19.5	19.1	3	15	1	29.6	-26.5
0	18	6	28.6	24.3	1	18	5	27.4	28.9	2	16	0	63.5	-64.1	3	15	3	20.5	19.8
0	19	2	36.7	-35.7	1	18	7	26.5	-30.7	2	16	2	77.1	-66.8	3	15	5	18.4	18.7
0	19	4	17.7	-19.3	1	19	1	50.0	-49.3	2	16	4	27.9	-28.8	3	15	7	24.3	-33.0
0	20	0	14.6	-14.9	1	19	3	38.3	40.7	2	16	8	37.4	-38.2	3	15	9	16.5	21.8
0	20	2	65.2	74.5	1	19	5	20.3	19.4	2	17	6	17.3	-17.0	3	16	1	147.2	138.4
0	20	4	24.1	26.0	1	20	1	25.5	-27.0	2	17	8	30.3	-32.2	3	16	3	37.8	35.3
0	21	2	30.2	-29.0	1	20	3	32.8	-34.1	2	18	2	16.4	14.0	3	16	5	66.0	-65.2
0	21	4	16.2	-18.8	1	20	7	22.4	25.1	2	18	4	54.1	55.8	3	17	5	31.1	38.9
0	21	6	43.6	39.4	1	21	5	31.3	-29.3	2	18	6	64.6	73.6	3	17	7	38.6	45.1
0	22	0	19.1	18.7	1	22	3	41.2	-35.5	2	19	2	19.4	-22.7	3	17	9	48.6	-48.1
0	22	2	28.5	-29.1	1	22	7	57.2	57.6	2	19	4	20.7	19.0	3	18	1	40.8	-44.5
0	22	4	36.5	-40.5	1	23	1	43.5	43.4	2	19	8	35.0	35.3	3	18	5	17.3	15.8
0	22	6	25.0	-20.8	1	23	3	39.1	-35.2	2	20	0	54.2	-56.2	3	18	7	20.8	-22.1
0	23	2	37.1	-31.8	1	24	1	25.5	-22.8	2	20	6	41.2	-46.6	3	18	9	24.9	23.2
0	24	0	61.9	60.7	1	24	5	25.0	29.0	2	20	8	20.7	19.4	3	19	1	46.0	-44.4
0	25	4	25.6	30.0	1	25	3	20.1	19.2	2	21	4	56.0	-52.5	3	19	3	20.5	18.5
0	26	0	79.9	-75.3	1	26	1	22.7	22.8	2	21	8	13.3	13.7	3	20	1	30.6	-30.6
1	1	1	99.9	121.7	2	0	0	88.9	153.9	2	22	0	56.9	63.6	3	20	3	31.2	-31.5
1	1	3	110.6	-134.6	2	0	2	74.1	-97.2	2	22	2	24.0	25.9	3	20	7	23.6	23.1
1	1	5	104.4	-91.6	2	0	4	189.2	-218.6	2	24	0	30.0	31.3	3	22	1	36.6	40.4

TABLE 4

(CONTINUED)

H	K	L	Fo	Fc	H	K	L	Fo	Fc	H	K	L	Fo	Fc	H	K	L	Fo	Fc
3	22	3	24.9	-23.5	4	18	4	14.0	-18.0	5	20	5	18.2	20.7	7	12	7	32.3	-37.7
3	22	5	21.4	-20.7	4	18	6	22.0	22.7	5	20	7	31.2	34.3	7	13	1	42.7	38.1
3	23	1	40.1	35.3	4	19	2	63.6	-62.7	5	22	3	24.2	-22.7	7	13	5	29.6	-30.2
3	23	3	40.8	-37.3	4	20	2	45.0	40.7	5	22	5	13.8	-18.6	7	13	9	30.9	29.9
3	23	5	24.9	-33.6	4	20	4	46.9	47.3	5	23	1	42.6	40.3	7	14	1	21.2	13.4
3	24	1	17.4	-19.9	4	21	4	30.3	-28.8	5	24	1	15.0	-16.3	7	14	5	16.4	12.9
3	24	3	27.0	24.6	4	21	6	42.6	40.2	6	0	4	155.4	-132.1	7	14	7	30.4	-33.6
3	25	1	25.2	24.5	4	22	2	22.2	-19.2	6	0	8	36.4	-33.2	7	15	1	29.4	-23.4
4	0	2	85.7	82.2	4	22	4	26.7	-28.5	6	1	8	98.1	-97.6	7	15	5	22.0	-23.8
4	0	4	24.5	-18.1	4	22	6	16.4	-20.2	6	2	4	16.4	12.7	7	16	1	39.9	37.8
4	0	10	40.8	37.4	4	24	0	75.6	71.0	6	2	6	20.5	-21.0	7	16	5	32.6	-33.4
4	1	2	46.0	47.6	4	24	2	16.0	14.7	6	2	8	68.0	60.3	7	16	7	8.5	10.1
4	1	4	116.3	116.9	4	24	4	19.9	-23.5	6	2	10	33.4	32.2	7	17	5	46.4	61.4
4	1	8	25.2	-17.6	5	1	3	68.3	-64.0	6	3	4	33.0	35.9	7	17	7	12.0	9.9
4	1	10	76.5	70.2	5	1	5	40.8	-36.9	6	3	6	20.5	-23.6	7	19	1	47.6	-34.7
4	2	2	43.6	-42.0	5	1	9	17.7	13.0	6	3	10	20.9	24.2	7	21	1	25.6	19.4
4	2	4	50.8	-58.2	5	1	11	28.7	23.4	6	4	4	52.8	-47.8	8	0	6	44.4	36.2
4	3	2	143.2	155.4	5	2	3	73.0	72.1	6	4	6	14.6	-15.7	8	0	8	18.0	14.4
4	3	4	15.9	-11.7	5	2	5	41.1	35.4	6	4	10	46.0	-44.6	8	0	10	18.0	22.5
4	3	6	148.0	-114.0	5	2	7	127.5	-98.6	6	5	6	35.9	-40.8	8	1	10	14.6	19.4
4	3	8	78.1	-67.1	5	2	11	69.9	47.7	6	5	10	51.4	-51.4	8	2	6	67.6	-68.2
4	4	2	59.8	56.1	5	3	5	64.2	-68.1	6	6	4	78.7	87.2	8	3	6	31.2	-36.6
4	4	4	44.3	42.7	5	3	7	40.4	33.7	6	6	6	94.3	103.5	8	3	8	30.7	-33.6
4	4	6	66.1	58.1	5	3	9	39.4	38.2	6	6	8	39.7	-31.4	8	3	10	17.1	-19.0
4	4	8	71.9	62.1	5	3	11	28.2	-25.1	6	7	6	59.1	63.5	8	4	6	25.3	27.9
4	5	2	16.6	-15.5	5	4	3	40.9	41.0	6	7	10	55.2	52.7	8	5	10	17.6	21.4
4	5	4	11.6	16.7	5	4	5	41.9	-37.9	6	8	0	132.4	-111.9	8	6	6	35.2	37.8
4	5	6	55.6	84.4	5	4	7	40.6	31.7	6	8	4	39.6	-45.2	8	6	8	50.3	-47.7
4	6	0	152.5	-190.2	5	4	9	35.0	-31.4	6	8	6	39.2	-39.7	8	6	10	31.3	-29.5
4	6	2	116.0	-119.3	5	4	11	15.9	-11.6	6	8	10	33.9	-39.4	8	7	6	17.3	-24.5
4	6	6	63.7	53.4	5	5	3	55.3	-57.6	6	9	4	35.9	-39.9	8	8	2	36.9	33.5
4	6	8	134.0	-120.4	5	5	5	52.0	51.6	6	9	6	20.9	22.6	8	8	8	39.9	34.3
4	6	10	75.9	-59.9	5	5	7	36.5	28.4	6	9	8	23.8	18.8	8	9	2	42.7	-40.5
4	7	2	81.1	-87.0	5	5	9	42.6	-36.8	6	9	10	41.9	-46.8	8	9	6	47.1	54.5
4	7	6	38.6	-28.8	5	5	11	15.5	-20.4	6	10	0	61.5	61.9	8	9	8	45.9	41.9
4	8	2	69.1	69.4	5	6	3	30.3	-38.9	6	10	8	32.8	32.4	8	10	6	39.5	-43.0
4	8	4	120.4	112.2	5	6	5	33.4	34.7	6	10	10	35.6	34.1	8	10	8	31.2	-26.7
4	8	6	17.5	19.7	5	6	9	17.1	-12.9	6	11	8	61.3	53.9	8	11	2	30.0	23.1
4	8	8	51.1	43.1	5	7	1	46.2	-37.3	6	12	0	110.7	111.1	8	11	6	15.5	-17.7
4	9	2	15.7	-11.7	5	7	3	27.0	22.3	6	12	4	84.3	-86.0	8	12	2	20.8	17.7
4	9	4	22.6	-23.0	5	7	5	63.6	64.8	6	12	8	30.2	-25.5	8	12	6	25.6	25.3
4	9	6	53.6	54.2	5	7	9	37.8	-31.5	6	13	8	85.6	-78.0	8	13	2	20.4	17.4
4	9	8	62.2	60.7	5	8	1	58.6	-62.1	6	14	0	30.0	-31.8	8	13	6	24.0	-25.7
4	9	10	25.6	26.9	5	8	3	45.3	-48.8	6	14	4	31.4	28.4	8	13	8	17.9	-17.3
4	10	0	14.2	10.3	5	8	5	37.4	35.7	6	14	6	23.3	-24.0	8	14	6	51.5	-56.4
4	10	2	27.8	-27.3	5	8	9	37.1	29.2	6	14	8	53.0	44.9	8	15	2	71.0	50.3
4	10	4	102.6	-94.6	5	9	5	45.4	-50.9	6	15	8	17.0	17.1	8	15	6	16.4	-23.6
4	10	6	83.0	-76.0	5	9	9	16.2	15.9	6	16	0	36.6	-33.7	8	16	6	31.6	38.5
4	10	10	17.4	16.6	5	10	3	41.5	-48.8	6	16	8	31.6	-25.2	8	18	2	42.6	-30.4
4	11	4	57.1	-56.0	5	10	5	41.1	-41.8	6	17	8	16.7	-19.8	8	19	2	22.7	-16.3
4	11	10	28.7	-34.6	5	10	7	83.7	76.1	6	18	0	20.0	22.2	8	20	2	23.3	24.0
4	12	0	175.5	189.1	5	10	11	48.7	-42.1	6	18	4	48.5	51.3	9	2	7	46.0	-45.7
4	12	2	37.4	39.1	5	11	1	97.2	94.6	6	18	6	48.1	53.1	9	3	7	37.2	-33.2
4	12	4	51.2	-50.7	5	11	3	62.7	-71.1	6	19	6	41.4	32.8	9	3	9	17.9	23.1
4	12	6	61.0	60.6	5	11	5	20.8	-24.5	6	20	0	78.6	-67.1	9	4	9	13.2	-20.3
4	12	8	24.2	21.9	5	11	11	28.9	25.7	6	20	6	24.5	-33.0	9	5	9	39.2	-49.6
4	12	10	22.0	27.7	5	12	1	51.5	-49.9	6	21	2	38.0	-27.0	9	8	3	20.7	-19.8
4	13	2	34.3	-33.5	5	12	5	46.8	52.5	6	21	4	26.0	-31.3	9	9	7	25.1	-24.3
4	13	4	72.5	81.8	5	13	5	41.8	-42.0	6	22	0	60.1	47.7	9	10	3	44.6	-45.3
4	13	8	16.6	-23.3	5	13	9	19.0	17.8	6	22	2	15.2	13.1	9	10	7	40.7	45.1
4	13	10	28.7	30.4	5	14	5	25.4	26.2	7	1	5	31.3	-27.4	9	12	3	26.3	25.4
4	14	0	126.1	-131.8	5	14	7	55.2	-47.8	7	1	9	22.3	24.2	9	14	3	44.2	30.4
4	14	2	20.1	-16.8	5	14	9	24.7	-23.3	7	1	11	15.8	19.6	9	15	3	15.4	14.6
4	14	4	20.8	20.6	5	15	3	41.1	44.6	7	2	5	54.3	51.3	10	1	8	19.1	-29.0
4	14	6	94.6	-93.1	5	16	1	60.4	57.7	7	2	7	60.4	-54.9	10	2	8	23.0	23.7
4	14	8	15.9	-19.4	5	16	3	31.6	35.0	7	2	11	25.2	28.4	10	6	4	26.3	23.8
4	15	2	107.1	99.6	5	16	5	34.2	-35.1	7	4	5	57.7	-55.9	10	7	4	25.8	23.8
4	15	4	25.6	-27.1	5	17	3	35.8	-42.2	7	4	9	15.3	-18.0	10	9	4	34.0	-30.5
4	15	6	53.5	-55.6	5	17	5	35.4	41.6	7	5	5	68.5	70.8	10	12	4	74.7	-50.6
4	15	8	33.7	-31.8	5	18	1	55.2	-46.7	7	5	9	47.6	-37.7	10	13	4	33.6	30.8
4	15	10	24.0	-20.2	5	18	3	24.4	-22.3	7	6	7	14.3	-16.0	10	14	4	28.3	21.3
4	16	0	25.3	25.1	5	18	5	25.2	29.4	7	7	5	18.4	19.0	11	3	5	29.3	-27.7
4	16	4	36.1	36.4	5	18	7	17.4	-19.5	7	8	5	26.0	27.9	11	4	5	20.2	-19.4
4	16	6	57.3	57.5	5	19	1	20.1	-22.0	7	9	5	18.3	-17.3	11	5	5	30.9	31.0
4	17	4	25.1	23.1	5	19	3	32.8	36.1	7	10	5	25.7	-30.3	11	6	5	18.7	15.1
4	17	8	31.3	6.1	5	19	5	16.4	21.7	7	10	7	60.7	70.0	11	7	5	24.9	21.8
4	18	0	35.9	-34.0	5	20	1	50.4	+34.6	7	11	1	29.9	25.6	11	9	5	13.9	-17.2
4	18	2	50.0	-50.3	5	20	3	37.4	-39.1	7	11	7	18.1	-22.1					

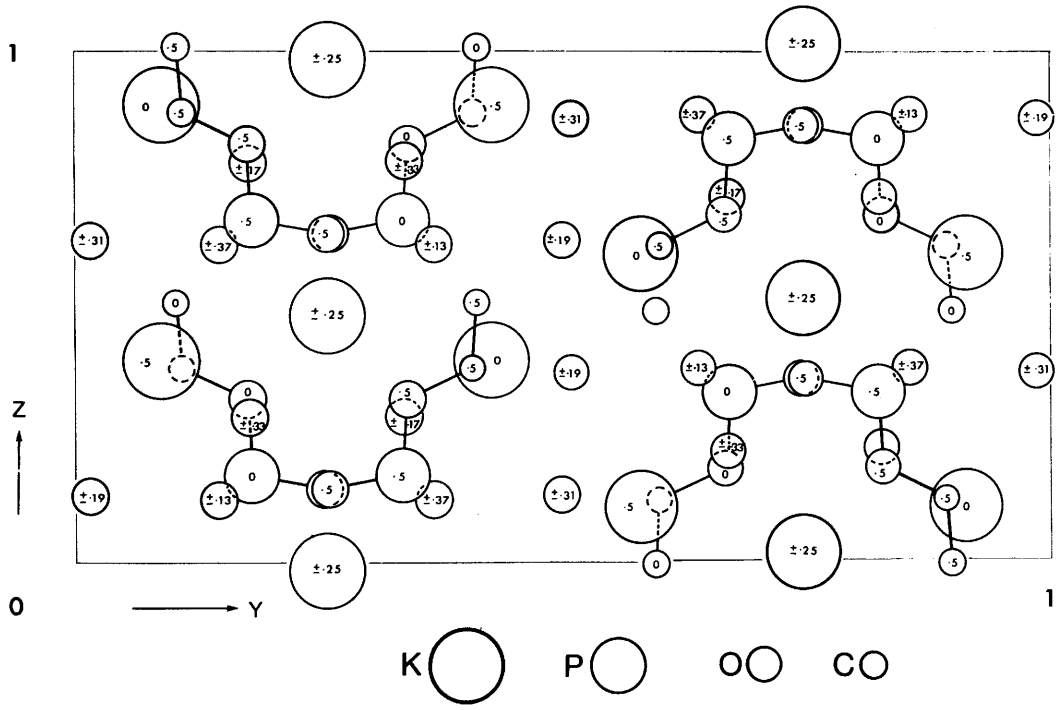

Figure 2.
a-axis projection of one unit cell.

in the true space group, but are related in pairs by the mirror plane in the pseudo-symmetric structure.

The Potassium Co-ordination

Each potassium ion is six co-ordinate, with K-O distances in the range 2·7-3·0 Å, and in addition each has two other K-O contacts of about 3·4 Å. The dimensions of the potassium co-ordination polyhedra are given in Table 5.

K(1), lying on a two-fold axis, (which is retained in the lower symmetry space group), has a highly distorted octahedral co-ordination. The four oxygens O(3), O(3)*, O(7), and O(7)* and the potassium ion are coplanar (this is not required by symmetry), with inter-bond angles of 78·7° (twice), 120·5°, and 82·2°. The angle between the two bonds to O(2) and O(2)*, above and below this plane, is only 112°, compared with 180° for an octahedral arrangement. If the two additional long bonds are considered the co-ordination approximates to that of a square anti-prism.

K(2), lying on the false mirror-plane, has a co-ordination approximating to a trigonal prism. If the two long bonds are also considered the oxygens lie at the corners of a highly distorted cube.

The mean K-O distance, assuming 6-co-ordination, is 2·86 Å. The individual K-O distances have standard deviations of about 0·01 Å, which would need to be

TABLE 5

BOND LENGTHS AND ANGLES AT THE POTASSIUM ATOMS

BOND	ANGSTROMS	BOND	ANGSTROMS
K(1) - O(5)	2.748	K(2) - O(5)	2.709
K(1) - O(3)	2.934	K(2) - O(4)	2.815
K(1) - O(2)	3.026	K(2) - O(3)	2.923
K(1) - O(1)	3.466	K(2) - O(4)**	3.416

ANGLE	DEGREES	ANGLE	DEGREES
O(5) - K(1) - O(5)*	82.2	O(5) - K(2) - O(5)*	75.5
O(5) - K(1) - O(3)	160.8	O(5) - K(2) - O(4)	91.9
O(5) - K(1) - O(3)*	78.7	O(5) - K(2) - O(4)*	148.5
O(5) - K(1) - O(2)	133.3	O(5) - K(2) - O(3)	79.5
O(5) - K(1) - O(2)*	99.1	O(5) - K(2) - O(3)*	110.1
O(3) - K(1) - O(3)*	120.5	O(4) - K(2) - O(4)*	84.0
O(3) - K(1) - O(2)	50.2	O(4) - K(2) - O(3)	95.3
O(3) - K(1) - O(2)*	94.9	O(4) - K(2) - O(3)*	131.9
O(2) - K(1) - O(2)*	112.0	O(3) - K(2) - O(3)*	51.0

increased slightly to take account of the additional uncertainty due to the pseudo-symmetry.

The ethyl phosphate group

The dimensions found for the ethyl phosphate group are given in Table 6. The standard deviations of the bond lengths, calculated for the pseudo-symmetric structure are 0·01 Å for P-O, 0·02 Å for C-O, and 0·04 Å for C-C. The C-C single bond distance of 1·35 Å is clearly very much too short. If we take the displacements of the carbon atoms given by the least squares refinement, and assume that C(1) and C(2) are displaced in opposite directions, the C-C bond length becomes 1·54 Å The C-O distance of 1·48 Å is about 0·05 Å longer than is usually found, but the difference cannot be regarded as significant. The indicated displacements from the mirror plane would slightly increase the dimension. The P-O(R) bond length of 1·55 Å is surprisingly short. It has a standard deviation of 0·01 Å, which would need to be increased slightly because of the uncertainty in the x-co-ordinates. The small displacements from the mirror plane indicated for the phosphorus and oxygen atoms would not greatly alter the P-O distances.

TABLE 6

DIMENSIONS OF THE ETHYL PHOSPHATE GROUP

BOND	ANGSTROMS
P - O(1)	1.549
P - O(2)	1.537
P - O(3)	1.514 (2x)
O(1) - C(1)	1.476
C(1) - C(2)	1.345

ANGLE	DEGREES
O(1) - P - O(2)	104.3
O(1) - P - O(3)	107.8 (2x)
O(2) - P - O(3)	112.0 (2x)
O(3) - P - O(3)*	112.4
P -O(1)-C(1)	120.2
O(1) -C(1)-C(2)	121.1

The mean P-O bond length is 1·523 Å, which may be compared with the mean of 1·515 Å found in calcium thymidylate (Trueblood, Horn, and Luzzati, 1961) and means of about 1·54 Å found in a number of $[ROPO_3H]^-$ structures (Kraut, 1961, Kraut and Jensen, 1963, Sundaralingham and Jensen, 1964, McCallum, Robertson, and Sim, 1959).

The Hydrogen Bonding and Oxygen Co-ordination

The oxygen atom O(1) is not co-ordinated to any atoms other than the phosphorus and carbon to which it is covalently bonded. Oxygen O(2), on the mirror-plane is 5-co-ordinate. It is bonded to phosphorus, to K(1) atoms above and below the mirror-plane, and accepts two hydrogen bonds from O(5) above and below the mirror plane.

Oxygen O(3) is also 5 co-ordinate. It is linked to phosphorus, to K(1) and to K(2), and accepts hydrogen bonds from O(4) and O(5).

The bond lengths and angles at the water molecules are given in Table 7. The water molecules O(4) are hydrogen bonded together in chains parallel to the z-axis. One of these hydrogen bonds of length 2·80 Å, lies across a two-fold axis in the higher symmetry space group. Since the hydrogen bond is too long to be

TABLE 7

CO-ORDINATION OF THE WATER MOLECULES

BOND	ANGSTROMS	BOND	ANGSTROMS
O(4) - O(3)	2.715	O(5) - O(2)	2.753
O(4) - O(4)*	2.856	O(5) - O(3)	2.778
O(4) - O(4)**	2.803	O(5) - K(1)	2.748
O(4) - K(2)	2.815	O(5) - K(2)	2.709
ANGLE	**DEGREES**	**ANGLE**	**DEGREES**
O(3) - O(4) - O(4)*	109.3	O(2) - O(5) - O(3)	105.1
O(3) - O(4) - O(4)**	100.4	O(2) - O(5) - K(1)	104.2
O(3) - O(4) - K(2)	123.9	O(2) - O(5) - K(2)	104.8
O(4)*- O(4) - O(4)**	144.0	O(3) - O(5) - K(1)	111.1
K(2) - O(4) - O(4)*	103.2	O(3) - O(5) - K(2)	125.2
K(2) - O(4) - O(4)**	74.9	K(1) - O(5) - K(2)	104.5

symmetrical, an ordered arrangement of the hydrogens would require a lowering of the symmetry. Each O(4) forms two hydrogen bonds to other O(4) molecules, one hydrogen bond to an O(3) of the phosphate group, and a bond to the potassium K(2). The arrangement is approximately tetrahedral.

The water molecules, O(5) also show tetrahedral co-ordination. Two hydrogen bonds are formed, to O(2) and O(3) of the phosphate group, and one bond is formed to each of the potassiums, K(1) and K(2).

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Chapter 7

Refinement of the Structure of S_3O_9

The γ-form of sulphur trioxide was examined by Westrik and MacGillavry (1941), who showed that it contained cyclic S_3O_9 molecules. Pascard and Pascard-Billy (1965) obtained fresh 3-dimensional data on this form, and carried out some refinement of the structure. Their published molecular dimensions, however, showed some anomalous features. There were some large and apparently significant differences between the lengths of chemically equivalent bonds. The six S-O bonds of the ring ranged in length from 1.53 to 1.65 Å, and the three equatorial S-O bonds were found to be 1.40, 1.33 and 1.40 Å, all with quoted standard deviations of 0.016 Å. Because of these rather implausible dimensions, their published data were subjected to further least-squares refinement.

Least-squares Refinement

The data used were the observed structure factors of Pascard and Pascard-Billy. An initial structure factor calculation, using their final parameters, indicated that the observed and calculated values for the 032 reflection were incorrectly given in Table 3 of their paper, and that the $3\bar{0}\ell$ reflections were given as 31ℓ in their table. The 032 reflection was omitted, and refinement of the

scale factor, co-ordinates, and temperature factors was carried out. The weighting scheme used was $w = 1/(7 + |Fo| + 0.02 |Fo|^2)$. Two cycles of full matrix isotropic refinement reduced the R-value to 0.142, and four cycles of block diagonal anisotropic refinement produced convergence, with a final R-value of 0.117. The scale factor obtained was 0.947, applied to the observed structure factors of Pascard and Pascard-Billy. The final co-ordinates are given in Table 1, together with the estimated standard deviations, and the temperature factors are given in Table 2.

Molecular Dimensions

A molecular vibration analysis was performed in order to correct the molecular dimensions for the effect of rigid body librations. The calculations were carried out on the K.D.F.9 computer, using a programme written originally for the Pegasus computer by A. Bujosa and D.W.J. Cruickshank. The principal values of the vibration tensor, T, are 0.0196, 0.0381, and 0.0277 Å^2, and of the libration tensor, w, 10.58, 24.46, and 14.39 degree^2. The direction of maximum vibration is approximately the crystallographic y-direction (direction cosines -0.175, 0.985, 0.010). The axis of maximum libration has direction cosines -0.227, 0.767, 0.600, which is approximately the S(3) - O(3) axis.

The corrections to the bond lengths obtained are not great, ranging from 0.005 to 0.008 Å. Table 3 gives the corrected and uncorrected bond lengths with their standard deviations, and the

TABLE 1

FINAL FRACTIONAL CO-ORDINATES

(E.S.D.s ARE GIVEN IN BRACKETS)

ATOM	x	y	z
S(1)	0.2082(17)	0.1302(6)	0.0819(4)
S(2)	0.0404(17)	0.3054(5)	-0.0732(4)
S(3)	0	0.3592(6)	0.1487(4)
O(1)	0.1234(49)	0.0075(18)	0.1032(15)
O(2)	0.4510(46)	0.1742(22)	0.0836(15)
O(3)	0.0682(40)	0.1632(12)	-0.0323(10)
O(4)	-0.1439(56)	0.2947(21)	-0.1584(13)
O(5)	0.2717(45)	0.3642(19)	-0.0821(13)
O(6)	-0.1168(34)	0.3600(15)	0.0273(11)
O(7)	0.2306(39)	0.4167(16)	0.1484(12)
O(8)	-0.2094(44)	0.3886(18)	0.2174(14)
O(9)	0.0258(51)	0.2105(13)	0.1617(11)

TABLE 2 TEMPERATURE FACTORS AND THEIR ESTIMATED STANDARD DEVIATIONS

ATOM	U11	U22	U33	2U23	2U31	2U12
S(1)	0.036(4)	0.041(3)	0.033(3)	0.006(5)	-0.007(5)	0.005(6)
S(2)	0.046(4)	0.039(3)	0.021(2)	0.006(4)	-0.003(5)	0.003(7)
S(3)	0.028(4)	0.052(3)	0.027(2)	-0.015(5)	-0.010(4)	0.003(6)
O(1)	0.074(18)	0.040(9)	0.057(10)	0.007(16)	0.000(23)	-0.009(19)
O(2)	0.055(19)	0.077(14)	0.049(10)	-0.012(19)	-0.035(19)	0.019(23)
O(3)	0.064(15)	0.023(7)	0.028(7)	-0.007(11)	-0.018(16)	0.001(16)
O(4)	0.073(16)	0.096(15)	0.032(8)	0.002(17)	-0.020(22)	-0.029(28)
O(5)	0.039(15)	0.066(12)	0.050(9)	0.020(16)	0.010(18)	0.002(19)
O(6)	0.020(10)	0.053(9)	0.032(7)	0.006(13)	-0.026(14)	0.001(17)
O(7)	0.033(13)	0.053(10)	0.044(9)	-0.013(15)	-0.002(16)	-0.032(19)
O(8)	0.043(14)	0.060(11)	0.056(11)	-0.018(17)	-0.002(19)	-0.012(19)
O(9)	0.057(12)	0.042(9)	0.027(7)	-0.012(13)	0.008(18)	-0.011(19)

TABLE 3 BOND LENGTHS AND ANGLES

BOND			UNCORRECTED	CORRECTED	E.S.D.
S(1)	-	O(3)	1.628	1.636	0.016
S(1)	-	O(9)	1.615	1.621	0.020
S(2)	-	O(3)	1.626	1.634	0.014
S(2)	-	O(6)	1.597	1.603	0.016
S(3)	-	O(6)	1.621	1.629	0.015
S(3)	-	O(9)	1.623	1.630	0.016
S(1)	-	O(1)	1.422	1.427	0.021
S(2)	-	O(4)	1.423	1.428	0.024
S(3)	-	O(8)	1.407	1.412	0.021
S(1)	-	O(2)	1.333	1.339	0.025
S(2)	-	O(5)	1.351	1.357	0.024
S(3)	-	O(7)	1.337	1.343	0.020
O(2)	-	O(5)	3.049	3.064	0.029
O(5)	-	O(7)	2.922	2.934	0.023
O(7)	-	O(2)	2.968	2.979	0.029

ANGLE					DEGREES	E.S.D.
O(3)	-	S(1)	-	O(9)	99.2	1.0
O(3)	-	S(2)	-	O(6)	98.6	0.8
O(6)	-	S(3)	-	O(9)	97.4	0.8
O(1)	-	S(1)	-	O(2)	128.1	1.5
O(4)	-	S(2)	-	O(5)	124.2	1.2
O(7)	-	S(3)	-	O(8)	125.0	1.2
O(1)	-	S(1)	-	O(3)	103.4	1.0
O(1)	-	S(1)	-	O(9)	102.1	1.1
O(4)	-	S(2)	-	O(3)	102.3	1.2
O(4)	-	S(2)	-	O(6)	105.9	1.3
O(8)	-	S(3)	-	O(6)	106.2	1.0
O(8)	-	S(3)	-	O(9)	103.0	1.1
O(2)	-	S(1)	-	O(3)	110.3	1.1
O(2)	-	S(1)	-	O(9)	109.9	1.3
O(5)	-	S(2)	-	O(3)	113.2	1.3
O(5)	-	S(2)	-	O(6)	109.5	1.0
O(7)	-	S(3)	-	O(6)	108.7	0.9
O(7)	-	S(3)	-	O(9)	112.9	1.2
S(1)	-	O(3)	-	S(2)	121.2	0.9
S(2)	-	O(6)	-	S(3)	122.4	1.1
S(3)	-	O(9)	-	S(1)	121.3	1.1

bond angles and standard deviations. The molecule does not deviate significantly from 3m symmetry.

The differences between chemically equivalent bond lengths originally reported are not confirmed. The mean S-O ring bond length is 1.626 Å, and the mean axial and equatorial bond lengths are 1.345 and 1.422 Å respectively. The difference in length between the ring and non-ring bonds is to be expected, but the 0.08 Å difference between the two types of non-ring bonds is difficult to understand. A small difference could perhaps be attributed to differing amounts of S- and p-character in the two types of bond, since all of the O(axial)-S-O angles are greater than tetrahedral, but a difference of the observed magnitude could hardly be explained in this way. This lends one to consider whether an error in the cell dimensions could cause this difference. The three axial S-O bonds have their largest component in the x-direction, and it is the a-dimension which has the greatest estimated error. The cell dimensions originally given by Westrik and MacGillavry were a = 5.3, b = 10.7, c = 12.3 Å. Pascard and Pascard-Billy give a = 5.13 $\pm$ 0.05, b = 10.82 $\pm$ 0.02, c = 12.40 $\pm$ 0.02. Thus the second determination increases the b- and c-dimensions by about 1%, but decreases the a-dimension by more than 3%. An error of 3 or 4% in the a-dimension would be sufficient to account for a large part of the observed difference between the axial and equatorial bonds.

A redetermination of the cell constants would be desirable. Figure 1 shows a projection of one molecule, with the corrected bond lengths indicated.

The Molecular Packing

Each molecule makes contacts of less than 3.4 Å with twelve neighbouring molecules. The molecules are arranged in a distorted hexagonal close-packed array, with the "hexagonal" axis parallel to the crystallographic y-axis. All inter-molecular distances of less than 3.5 Å are listed in Table 4. Each molecule makes a total of 50 contacts of less than 3.5 Å with atoms of its 12 neighbours.

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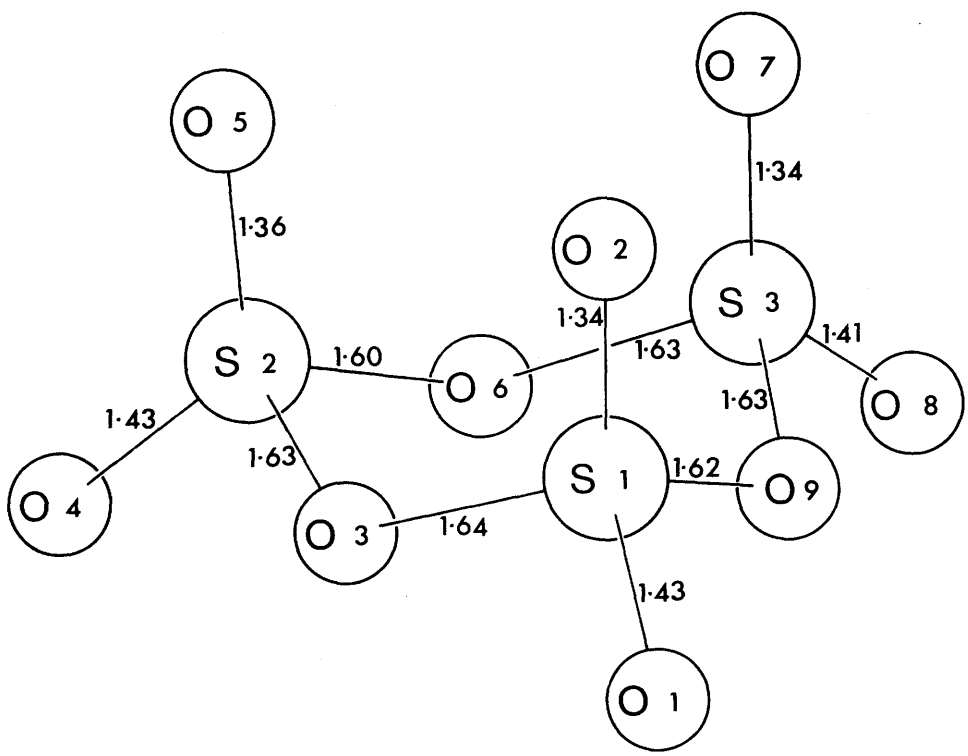

Figure 1.
Projection of one molecule, with corrected bond lengths.

TABLE 4 INTERMOLECULAR CONTACTS

x, y, z	to	1+x, y, z	and	
x-1, y, z	to	x, y, z.		
O(7)	-	O(8)	3.013	
O(2)	-	O(6)	3.073	
O(2)	-	O(9)	3.129	
O(5)	-	O(4)	3.232	
O(2)	-	O(8)	3.342	
O(5)	-	O(6)	3.418	
O(2)	-	O(3)	3.479	
x, y, z	to	x-1/2, 1-y, -z	and	
1/2+x, 1-y, -z	to	x, y, z.		
O(6)	-	O(5)	3.114	
O(8)	-	O(5)	3.159	
O(4)	-	O(7)	3.190	
S(3)	-	O(5)	3.318	
O(6)	-	O(7)	3.346	
O(7)	-	O(5)	3.440	
x, y, z	to	1/2+x,1/2-y,1/2+z	and	
x-1/2,1/2-y,z-1/2	to	x, y, z.		
O(9)	-	O(4)	2.801	
O(2)	-	O(4)	3.254	
O(7)	-	O(4)	3.375	
S(1)	-	O(4)	3.406	
S(3)	-	O(4)	3.440	
x, y, z	to	1/2+x, -y, -z	and	
x-1/2, -y, -z	to	x, y, z.		
O(1)	-	O(3)	3.065	
O(2)	-	O(1)	3.164	
S(1)	-	O(1)	3.468	
x, y, z	to	x,y-1/2,1/2-z	and	
x, y+1/2,1/2-z	to	x, y, z.		
O(1)	-	O(8)	3.085	
O(1)	-	O(7)	3.280	
x, y, z	to	1/2+x,1/2-y,z-1/2	and	
x-1/2,1/2-y,1/2+z	to	x, y, z.		
O(3)	-	O(8)	3.354	
O(4)	-	O(8)	3.358	

Chapter 8

General Discussion

In this chapter an attempt is made to review the results obtained in this work in so far as they contribute to our understanding of π-bonding in second row elements.

The results of Chapter 2 on the aluminium-nitrogen tetramer show that in this compound the aluminium forms four σ-bonds, and is not p-p π-bonded as was originally thought possible. There, is therefore, as in the case of silicon, no evidence for p-p π-bonding.

The refinement of the hemimorphite structure (Chapter 4), and of sodium pyrophosphate (Chapter 5), together with the accurate electron diffraction study of chlorine heptoxide by Beagley(1965) and the earlier results of Lynton and Truter (1960) on potassium pyrosulphate, permit a comparison of the dimensions of the iso-electronic series of X_2O_7 groups. The results of a refinement of thortveitite (Cruickshank, Lynton, and Barclay, 1962) provide dimensions of a linear Si_2O_7 group, and the analyses of Calvo (1965) of zinc and magnesium pyrophosphates provide dimensions of linear P_2O_7 groups. The more important dimensions of these X_2O_7 groups are collected in Table 1.

Table 1 Dimensions of X_2O_7 groups

Compound	Bridge Bond	Mean Terminal Bond	Bridge Angle	Mean Terminal Angle
Cl_2O_7	1·709(2) Å	1·405(1) Å	119°	115°
$K_2S_2O_7$	1·645(5)	1·437(4)	124	114
$Na_4P_2O_7 \cdot 10H_2O$	1·612(4)	1·513(4)	130	113
$Mg_2P_2O_7$	1·557(2)	1·539(6)	180	113
$Zn_2P_2O_7$	1·569(5)	1·555(9)	180	112
$Zn_4Si_2O_7(OH)_2H_2O$	1·626(5)	1·624(6)	150	111
$Sc_2Si_2O_7$	1·607(7)	1·626(12)	180	112

The most obvious trend in the iso-electronic series of X_2O_7 groups is the diminishing difference between the two bond lengths, accompanied by an opening of the angle at the bridging oxygen, in going from chlorine to silicon. If we ignore for the moment the results on the linear X_2O_7 groups, the differences between the bridge and terminal bond lengths are 0·3 Å for the chlorine compound, 0·2 Å for sulphur, 0·1 Å for phosphorus, and for silicon the two types of bond are of the same length. As noted by Beagley (1965), the bridging Cl-O distance is that of a pure single bond. In Cruickshank's (1961) discussion of π-bonding it was proposed that the total π-bond order of the four tetrahedral X-O bonds should be two. The terminal Cl-O bonds should therefore have π-bond orders of $^2/_3$. In Si_2O_7 where all bond lengths are equal the π-bond orders should be $^1/_2$. Two effects are probably operative in producing this equalisation of π-bond orders. Firstly, the decreasing electronegativity of the second row element causes a shift of the bonding electrons towards the bridging oxygen. This would be energetically favoured by an increase in s-character of the σ-bonding orbitals of the oxygen, achieved by an opening of the bridge angle. This would then allow a greater participation of the lone pair electrons of the bridge oxygen in the π-bond

system, and a consequent equalisation of the bridge and terminal bonds. Secondly, the increasing charge on the X_2O_7 group will be offset by an increased covalent character in the bonds between the terminal oxygens and the cations. This will reduce the availability of lone pair electrons for π-bonding, again tending to equalise the lengths of the two types of bond. For Cl_2O_7 these two effects would be minimal, and the bridge oxygen could be Sp^3 hybridised, with no participation of its lone pairs in π-bonding. In the case of Si_2O_7 the two effects together are presumably sufficient to equalise the π-bond orders.

For the three structures which have linear X_2O_7 groups, crystal packing forces probably produce an additional opening out of the bridge angle. A further equalisation of the bond lengths should then occur, as is observed. In the case of thortveitite the terminal bonds are actually slightly longer than the bridge bonds.

Dimensions are available for the iso-electronic series of X_3O_9 groups. The refinement described in Chapter 7 gives results for the S_3O_9 molecule. The structures of $LiK_2P_3O_9.H_2O$ (Banes and Ondik, 1962) and of $Na_3P_3O_9$ (Ondik, 1965) provide dimensions for the $P_3O_9^{3-}$ anion. Dr. K.F. Fischer has kindly provided

dimensions for the Si_3O_9 group from his refinement of Benitoite, $BaTiSi_3O_9$. These results are collected in Table 2.

Table 2 Dimensions of X_3O_9 groups

Compound	Mean Ring Bond	Mean Non-Ring Bond	Mean X-O-X Ring Angle	Mean O-X-O Ring Angle	Mean O-X-O Non-Ring Angle
S_3O_9	1·626(7) Å	1·384(10) Å	122°	98°	126°
$Na_3P_3O_9$	1·615(2)	1·482(3)	127	101	120
$LiK_2P_3O_9$	1·611(5)	1·480(5)	129	100	121
$BaTiSi_3O_9$	1·639(3)	1·605(2)	133	107	113

The same trends as were noted for X_2O_7 groups are seen here. There is an opening out of the X-O-X angle in going from sulphur to silicon. Since the structures have a six-membered ring, the sum of the X-O-X and O-X-O ring angles cannot exceed 240°. This maximum is achieved in the Si_3O_9 structure, where the X-O-X angle is 133° and the ring is planar. Since the angle cannot open out any further, the complete equalisation of Si-O bonds found in Si_2O_7 cannot occur and a difference of 0·03 Å remains. For S_3O_9, where the ring is considerably puckered, the difference is 0·24 Å.

The rather unsatisfactory results of the $K_2EtPO_4.4H_2O$ structure determination (Chapter 6) do not permit

any detailed discussion of $ROXO_3$ structures.

In Chapter 2 the dimensions of the metasilicate chain in Na_2SiO_3 were compared with those of other metasilicates, and the effect of varying electronegativity of the cations was noted. A comparison between metasilicate and metaphosphate structures would be of interest. The structure of rubidium metaphosphate was refined by Cruickshank (1964). The bridge bonds were of mean length 1·62 Å, and the non-bridge bonds 1·49 Å. The P -- O - P angle was 129°. Here, again there is an opening of the bridge angle in going from phosphorus to silicon, accompanied by an equalisation of the bond lengths.

In conclusion, it seems that the simple explanation of the bond lengths in terms of isolated anions, and their π-bond orders, is inadequate. For silicates, in particular, the bonds to the cations play a significant role, and it cannot be said with any certainty that d-p π-bonding in silicate structures does occur.

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